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Influence of Mixing Method and Mixing Ratio of Imitation Dry Sludge Powder on Compressive Strength of Geopolymer Mortar

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Abstract: This study experimentally examined how the mixing method of geopolymer mortar by the powder addition method and the aqueous solution addition method and the mixing ratio of imitation dry sludge powder affect the compressive strength of resultant geopolymer mortar. It was found that regardless of the type of fly ash, the mixing method and the addition method of Na_2SiO_3 had no effect on the flow value, air content, and compressive strength. While using 3.0 mol/L Na_2SiO_3 aqueous solution, a maximum compressive strength of approximately 35 N/mm^2 was obtained at normal temperatures, when the fly ash used has a specific surface area of approximately 7000 cm^2/g and the mixing ratio of imitation dry sludge powder is up to 10.0%.

Keywords: Geopolymer, Sodium metasilicate, Mixing method, Sludge, Anhydrous citric acid, Compressive strength

1. Introduction

The amount of coal ash generated from Japanese electrical power plants has been increasing, exceeding 12 million tons annually in recent years [1]. For effective use of coal ash, many researchers have tried to use fly ash (FA) as an admixture for concrete. However, only 3.5% of the generated coal ash is actually

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used for this purpose [2]. On the other hand, over 300,000 tons of concrete sludge is generated per year in Japan due to the treatment of return concrete. However, most of the concrete sludge is landfilled as industrial waste [3].

Based on this background, from the viewpoint of reducing CO_2 emissions and effectively using industrial by-products, research on geopolymers (GPs) for obtaining polycondensate of alumina silica powder and an alkaline solution has attracted attention [4]. Dr. Inukai conducted effective use of FA and concrete sludge [imitation dry sludge powder (DSP)], and fundamental research on the GPs. They reported that it is possible to increase the compressive strength even curing at normal temperature by using finely ground FA and a high-concentration sodium metasilicate aqueous solution (Na_2SiO_3) for a GP [5-8]. Therefore, the mixing method including the addition method of Na_2SiO_3 needs to be examined in more detail [7]. Further, almost no studies have effectively used sludge in GPs [5, 9], and hence the mixing ratio of DSP also needs to be optimized.

In an experiment, the effect of the type of FA and the mixing method on the compressive strength of GP mortar was examined by the powder addition method and the aqueous solution addition method. In another experiment, the influence of the mixing ratio of DSP on the compressive strength of GP mortar was examined. In a third experiment, anhydrous citric acid is added as a setting retarder (ST), and its effects on the compressive strength of GP mortar was examined.

Table 1 Experimental Factors (Exp.1)

Factors	Levels
FA type	FAI, FAII, FAII5, FAII7
Mixing method	PM1, PM2, PM3, PM4 PM5, PM6, AW1, AW2

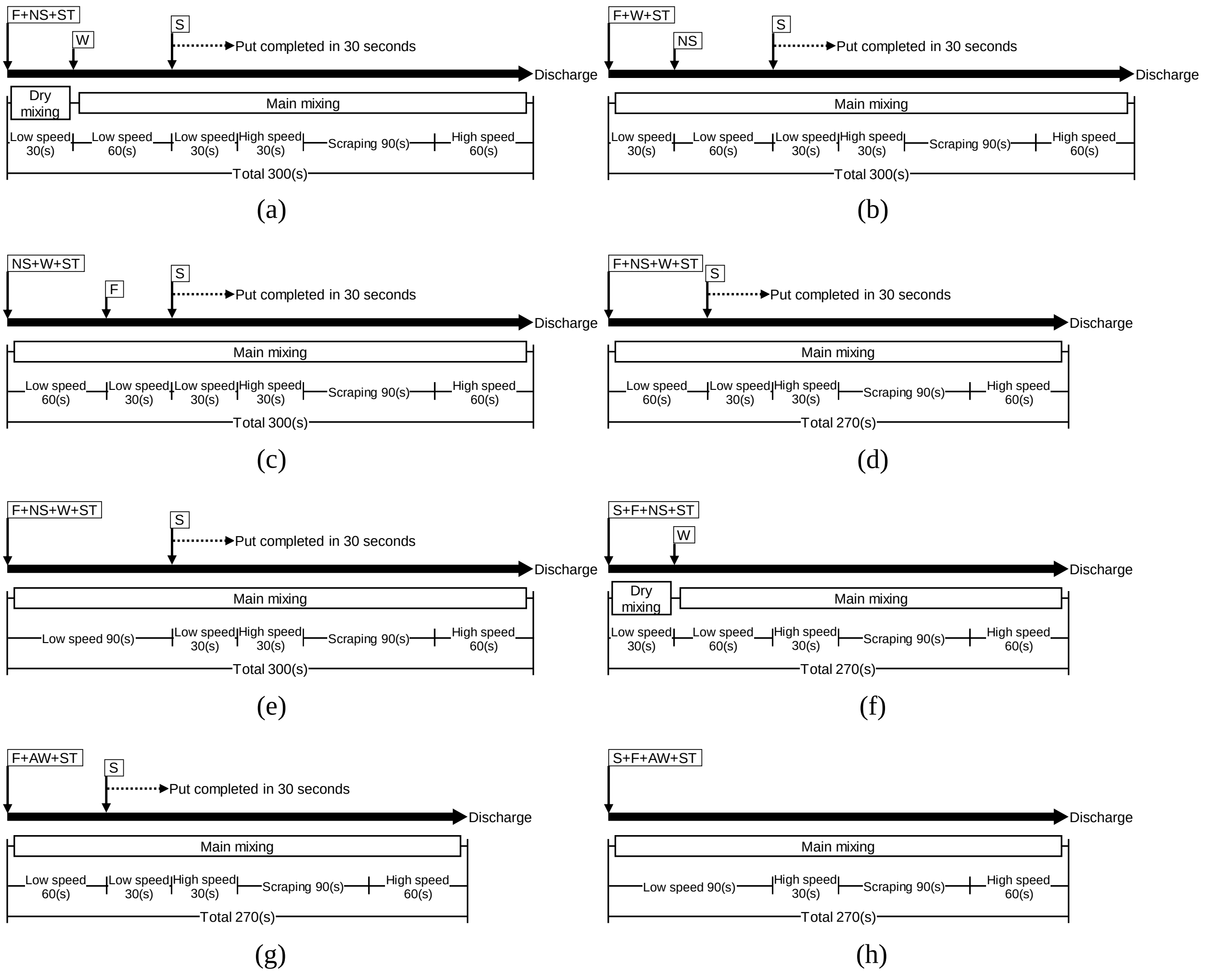


Figure1 Mixing Method (Exp.1–3)

2. Influence of Type of FA and Mixing Method on Compressive Strength of GP Mortar (Exp. 1)

2.1 Overview of Experiment

2.1.1 Experimental Factors

Table 1 shows the experimental factors, while Figure 1 shows the mixing method. The mixing method was JIS R 5201 "Physical Testing Methods for Cement" as reference, and six types of the powder addition method and two types of the aqueous solution addition method were used.

2.1.2 Used Materials and Mix Proportion

The materials used are listed in Table 2. The chemical composition measured with X-ray fluorescence (XRF) and the amount of glass phase in FA measured using X-ray diffraction (XRD) are reported in Table 3. The crystal minerals (quartz and mullite) were quantified from the calibration curve, and the amorphous phase was calculated from the difference between the measured value and the total amount. According to Table 3, all four types of FA contained similar amounts of glass phase. FAI contained approximately 6–10% less SiO_2 and approximately 4–6% more Al_2O_3 than FAII.

Table 2 Used Materials (Exp.1–3)

Material names	Marks		Types	Physical properties
Fly ash	F	FAI	A power plant Fly ash JIS type I Fine grinding: Absence	Blaine (cm^2/g): 5360 Density (g/cm^3): 2.43
		FAII	A power plant Fly ash JIS type II Fine grinding: Absence	Blaine (cm^2/g): 3980 Density (g/cm^3): 2.26
		FAII5	A power plant Fly ash JIS type II Fine grinding: Presence	Blaine (cm^2/g): 5213 Density (g/cm^3): 2.47
		FAII7	A power plant Fly ash JIS type II Fine grinding: Presence	Blaine (cm^2/g): 7088 Density (g/cm^3): 2.52
Fine aggregate	S		Dry Silica Sand (No.4, No.5)	Absolute dry density (g/cm^3): 2.64 Mixing ratio 1:1
Water	W		Tap water	-
Alkaline additives	NS		Sodium metasilicate	Density (g/cm^3): 2.61
Setting retarder	ST		Anhydrous citric acid ($C_6H_8O_7$)	Density (g/cm^3): 1.66

Table 3 X-ray Analysis Results of Materials Used (Exp.1–3)

(%)

Materials	Chemical compositions						Glass phase amount
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Ig.loss	
FAI	56.0	26.2	6.0	3.3	1.1	3.3	60.3
FAII	65.6	20.9	4.1	2.3	1.2	2.9	59.5
FAII5	62.1	22.5	4.6	2.7	1.4	2.5	62.3
FAII7	61.8	22.5	4.8	2.7	1.4	2.5	61.2

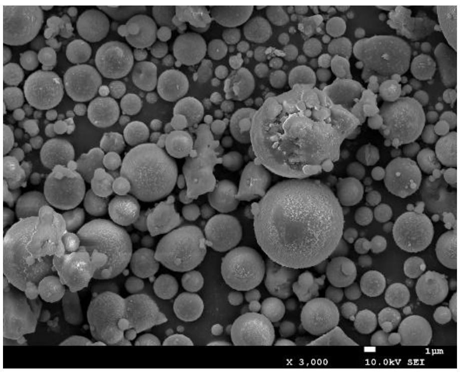
Image 1 displays the SEM images of four types of FA at 3000× magnification. According to Figure 2, FAI, FAII5, and FAII7 have narrow particle size distributions with a single peak at around 6–10 μm. On the other hand, FAII has a wider particle size distribution, and there are a main peak at around 20 μm and a smaller peak at approximately 100 μm. This trend is consistent with the specific surface area (Table 2) and Image 1. In addition, Image 1 shows that FAI and FAII contain mostly spherical particles, while FAII5 and FAII7 contain crushed particles from the fine grinding.

Table 4 shows the mix proportion of the powder addition method, and Table 5 shows the mix proportion of the aqueous solution addition method. In Table 4, AW indicates W+Na_2SiO_3. The mix proportion was all calculated for an AW/F ratio of 50% and the air content of 2%. The added amount of Na_2SiO_3 was set to 3.0 mol/L in terms of the concentration of Na_2SiO_3 aqueous solution, since this concentration led to the highest compressive strength in a previous study [7]. The concentration of the Na_2SiO_3 aqueous solution was also set to 3.0 mol/L. Meanwhile, the addition ratio of ST was fixed at 2.0%, based on previous studies [6-8].

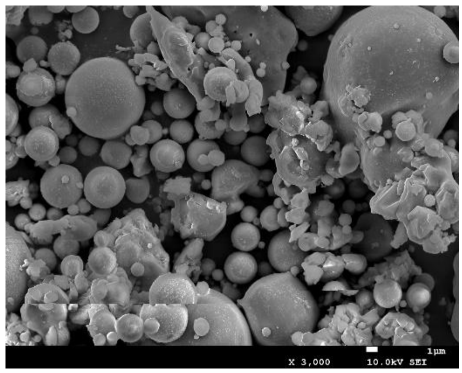
2.1.3 Mixing and Flow Tests

The mixing test procedures are illustrated in Figure 1. The flow test was carried out in accordance with JIS R 5201 “Physical Testing Methods for Cement”. The batch mixing volume was 1 L. Previously reported experimental results [6-8] indicated that it is impossible to mix FA Ⅱ within the time shown in Figure 1.

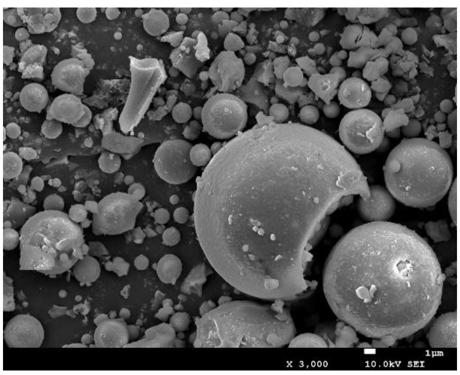
Therefore, when using this FA, the mixing time was extended by 1 minute.



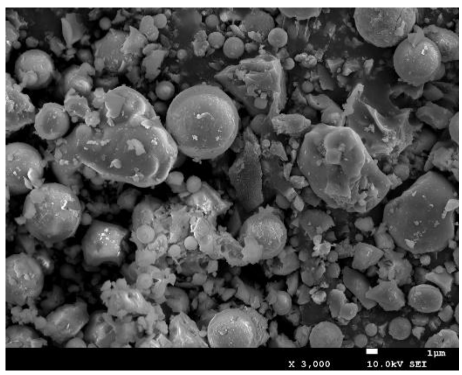
(a) FA Ⅰ



(b) FA Ⅱ



(c) FA Ⅱ 5



(d) FA Ⅱ 7

Image 1 SEM Images of FA at 3000 × (Exp.1–3)

2.1.4 Air Content Tests

The air content was measured in accordance with JIS A 5002 “Lightweight aggregates for structural concrete” (5.12.d Measurement of weight per unit volume of mortar), and was calculated in accordance with JIS A 1116 “Method of test for unit mass and air content of fresh concrete by mass” (6.2 Air content). The test material was created in two layers. Each layer was compacted for 30 s by vibration using a table vibrator.

2.1.5 Compressive Strength Tests

The compressive strengths were measured in accordance with JIS A 1142 “Method of test for fine aggregate containing organic impurities by compressive strength of mortar”. The test material was created in two layers. Each layer was compacted by vibration using a table vibrator for 30 s. After placing the specimens in molds, their upper surfaces were sealed with clear film, and they were cured for 28 days at 20 ℃.

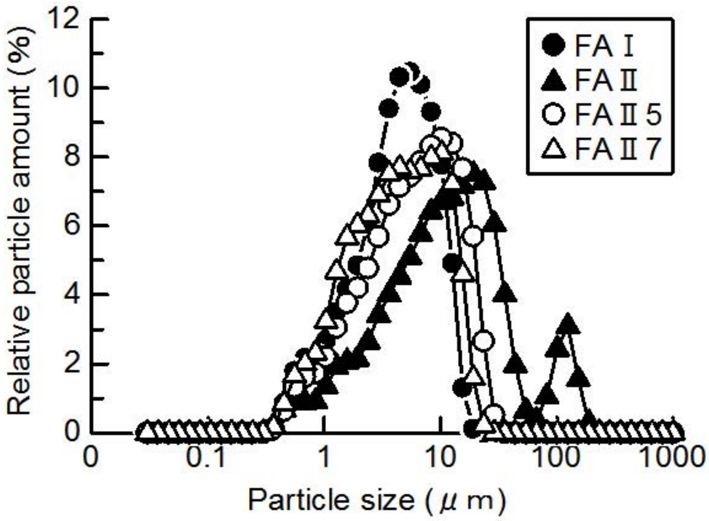


Figure 2 Particle Size Distribution of FA

Table 4 Mix Proportion of Powder Addition Method (Exp.1)

NS added amount*)	FA types	Flow	Air (%)	AW/F (%)	S/F	Unit weight(kg/m^3)				Weight (kg)
						F	AW		S	ST
							W	NS		
3.0	FAI	190 ± 20	2	50	2.21	580	203	87	1283	11.6
	FAII				1.50	680	238	102	1021	13.6
	FAII5				2.08	600	210	90	1250	12.0
	FAII7				1.85	640	224	96	1181	12.8

*)Converted to NSaq concentration (mol/L)

Table 5 Mix Proportion of Aqueous Solution Addition Method (Exp.1)

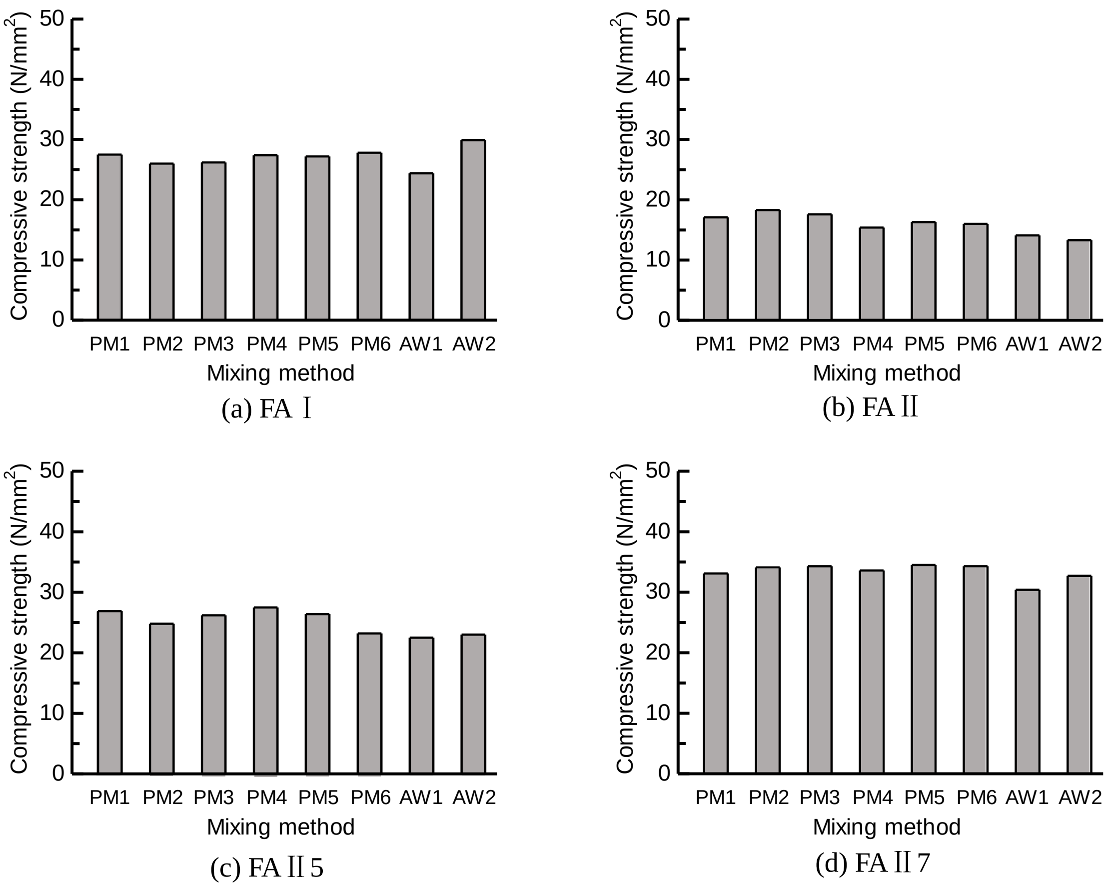
NSaq concentration (mol/L)	FA types	Flow	Air (%)	AW/F (%)	S/F	Unit weight(kg/m^3)			Weight(kg)
						F	AW	S	ST
3.0	FAI	190 ± 20	2	50	2.21	580	290	1280	11.6
	FAII				1.50	680	340	1021	13.6
	FAII5				2.08	600	300	1250	12.0
	FAII7				1.85	640	320	1181	12.8

2.2 Results and Discussions

Table 6 shows the measurement results for flow value and air content. The mixing method had no effect on the flow value. PM4 and PM5 with different mixing times also showed almost the same flow values. Therefore, within the range of this experiment, the flow value is regarded as independent of the mixing time. The presence or absence of finely ground FA had little effect, but the flow value tended to increase when FAII7 was used.

Table 6 Measurement Results for Flow Value and Air

Mixing method	Flow				Air (%)			
	FA types				FA types			
	FAI	FAII	FAII5	FAII7	FAI	FAII	FAII5	FAII7
PM1	186	190	186	202	2.9	0.6	2.7	2.2
PM2	171	180	188	187	2.4	0.8	2.5	1.3
PM3	187	182	183	200	1.7	0.9	2.4	1.7
PM4	178	190	186	209	2.4	0.8	2.2	1.9
PM5	183	192	189	209	1.9	0.5	3.1	2.9
PM6	185	174	181	198	2.1	1.2	3.0	2.4
AW1	188	183	189	210	2.4	0.9	3.7	2.7
AW2	193	203	188	206	2.3	1.3	3.4	2.3



(a) FA Ⅰ (b) FA Ⅱ (c) FA Ⅱ 5 (d) FA Ⅱ 7

Figure 3 Relationship between Compressive Strength and Mixing Method

Similarly, the mixing method had no effect on the air content. The amount of entrapped air tended to increase when FA with a larger specific surface area was used, which is consistent with a previous study [7]. However, whereas the correlation in Ref. [7] was monotonous, here the air content decreased in some cases with FAII7, which has the largest specific surface area.

Figure 3 shows the relationship between the compressive strength and the mixing method, confirming that the mixing method had no effect for any type of FA. In addition, between PM4 and PM5 with different mixing times, the compressive strength was almost the same. Therefore, within the range of this experiment, the compressive strength is regarded as independent of the mixing time. This trend is similar to that described in another study [10]. On the other hand, focusing on the type of FA, FAII7 having the largest specific surface areas showed the highest compressive strength with a maximum value of approximately 35 N/mm^2. For the other FAs, the compression strength was generally related to the specific surface area of the FA, a trend that is similar to Ref. [7]. From the results in Exp. 1, it can be considered that the material input order and the mixing time have less effects, because the dissolution of Na_2SiO_3 is considered to have priority in the powder addition method. In addition, even in case of the powder addition method, Na_2SiO_3 is considered to dissolve at the end of the mixing, and so its addition had same result as the aqueous solution addition method.

Table 7 Mix Proportion of Powder Addition Method (Exp.2)

NS added amount*)	FA types	DSP (B**)×%)	Flow	Air (%)	AW/B (%)	S/F	Unit weight(kg/m^3)					Weight (kg)
							F	DSP	AW		S	
									W	NS		ST
3.0	FAII7	0	190 ± 20	2	50	1.85	640	0	224	96	1181	12.8
		2				1.89	627	13	224	96	1184	12.8
		4				1.92	614	26	224	96	1179	12.8
		6				1.95	602	38	224	96	1176	12.8
		8				2.00	589	51	224	96	1176	12.8
		10				2.04	576	64	224	96	1173	12.8

*)Converted to NSaq concentration (mol/L)
**)B:(F+DSP)

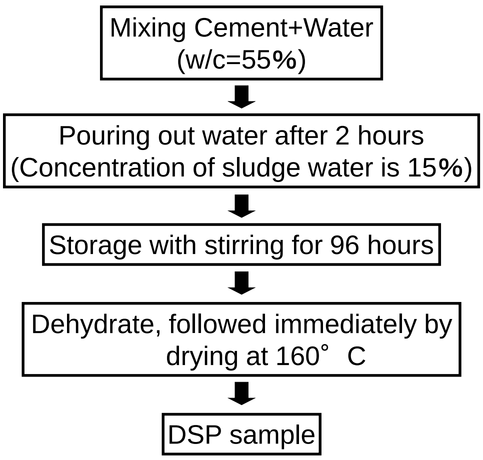


Figure 4 Manufacturing Method of DSP (Exp.2)

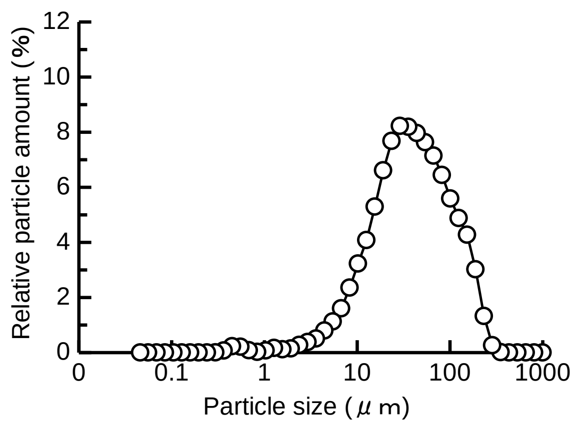


Figure 5 Particle Size Distribution of DSP (Exp.2)

3. Influence of Mixing Ratio of DSP on Compressive Strength of GP Mortar (Exp. 2)

3.1 Overview of Experiment

3.1.1 Experimental Factors

The experimental factor was the mixing ratio of DSP in FA Ⅱ 7(0, 2, 4, 6, 8, and 10%).

3.1.2 Used Materials and Mix Proportion

The materials used were the same as in Exp. 1 (refer to Table 2), and Table 7 shows the mix proportion of the powder addition method. Figure 4 shows the manufacturing method of DSP, which had a narrow particle distribution peaking at around 30 μm (Figure 5).

3.1.3. Mixing and Flow Tests

The mixing test was carried out in accordance with PM3 shown in Figure 1(c). The flow tests were carried out in the same manner as in Exp. 1.

3.1.4. Air Content Tests

The air content tests were carried out in the same manner as in Exp. 1.

Table 8 Measurement Results for Flow Value and Air Content (Exp.2)

DSP mixture ratio (%)	Flow	Air (%)
0	200	1.7
2.0	188	1.5
4.0	190	1.5
6.0	193	2.2
8.0	195	1.9
10.0	185	1.7

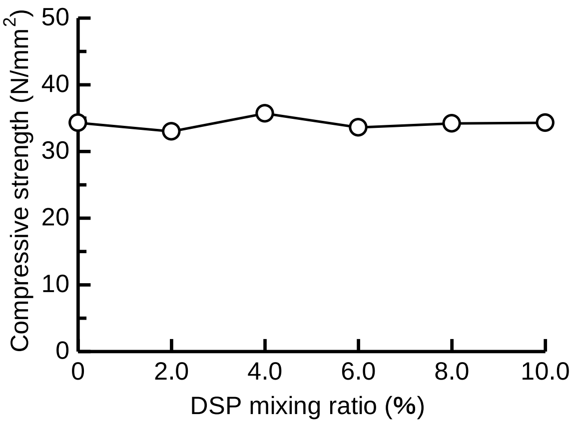


Figure 6 Relationship between Compressive Strength and DSP Mixing Ratio (Exp.2)

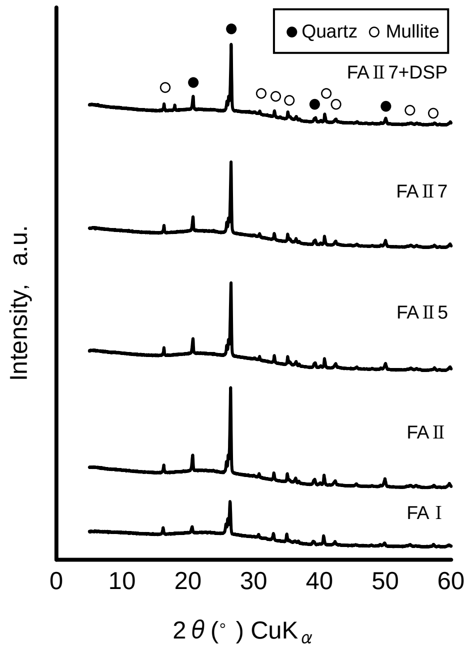


Figure 7 XRD Patterns of Hardened Body of GP Paste Produced Using FA and DSP (Exp.2)

3.1.5. Compressive Strength Tests

The compressive strength was measured in the same manner as in Exp. 1.

3.2. Results and Discussions

Table 8 shows the measurement results for flow value and air content, which shows no obvious effect from the mixing ratio of DSP. Figure 6 also confirms that the DSP mixing ratio had no influence on the compressive strength. This tendency is different from a previous study [5] that showed a negative correlation between the two when using the aqueous solution addition method. Although more detailed investigation is needed in the future, it may be attributed to the amount of CaO contained in DSP and the different mixing method. However, within the range of this experiment, it is considered that DSP can be used effectively if its mixing ratio is in the range of 10.0%.

Figure 7 shows the XRD pattern for the hardened body of GP paste after 28 days of curing, manufactured using FA and DSP and under the condition of AW/(F+DSP) = 50%. When the GP was produced using only FA, the XRD peaks of quartz (SiO_2) and mullite ($Al_6O_{13}Si_2$) are displayed. Since these peaks come from the FA powder, it means that the FA particles remain unreacted after mixing and curing. This trend is similar to a previous report [11], and there is no effect from using finely ground FA. In the XRD pattern using DSP, peaks other than those of quartz and mullite were confirmed at around 18°. However, this is merely due to the DSP. In addition, a comparison of all XRD patterns failed to show any influence from the addition of DSP on the compressive strength. To clarify the effect of DSP addition, it is necessary to compare the XRD patterns for different mixing ratios.

4. Influence of Addition Ratio of ST on Compressive Strength of GP Mortar (Exp. 3)

4.1 Overview of Experiment

4.1.1 Experimental Factors

The experimental factor was the addition ratio of ST in FAⅡ7(0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0%).

4.1.2 Used Materials and Mixing Proportion

The materials used were the same as in Exp. 1 (refer to Table 2), and Table 9 shows the mix proportion of the powder addition method.

Table 9 Mix Proportion of Powder Addition Method (Exp.3)

NS added amount*)	FA types	ST addition ratio (%)	Flow	Air (%)	AW/F (%)	S/F	Unit weight(kg/m^3)				Weight (kg)
							F	AW		S	
								W	NS		ST
3.0	FAII7	0	190 ± 20	2	50	1.85	640	224	96	1181	0
		0.5				1.85	640	224	96	1181	3.2
		1.0				1.85	640	224	96	1181	6.4
		1.5				1.85	640	224	96	1181	9.6
		2.0				1.85	640	224	96	1181	12.8
		2.5				1.85	640	224	96	1181	16.0
		3.0				1.85	640	224	96	1181	19.2

*)Converted to NSaq concentration (mol/L)

4.1.3. Mixing and Flow Tests

Table 10 Measurement Results for Flow Value and Air Content (Exp.3)

ST addition ratio (%)	Flow	Air (%)
0	190	2.1
0.5	187	1.8
1.0	191	2.0
1.5	192	2.0
2.0	200	1.7
2.5	193	2.3
3.0	198	2.3

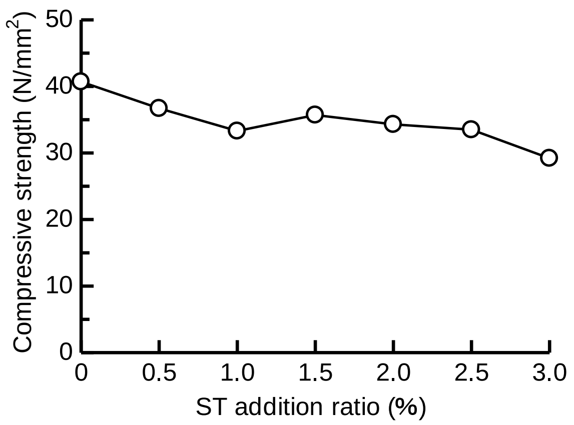


Figure 8 Relationship between Compressive Strength and ST Addition Ratio (Exp.3)

The mixing test was carried out in accordance with PM3 shown in Figure 1(c). The flow tests were carried out in the same manner as in Exp. 1.

4.1.4. Air Content Tests

The air content tests were carried out in the same manner as in Exp. 1.

4.1.5. Compressive Strength Tests

The compressive strength was measured in the same manner as in Exp. 1.

4.2. Results and Discussions

Table 10 shows the measurement results for flow value and air content, which shows no obvious effect from the mixing ratio of DSP, which shows no obvious effect from the addition ratio of ST. Figure 8 shows the relationship between the compressive strength and the addition ratio of ST. The compressive strength tended to decrease when the ratio of ST increased, approximately 10 N/mm^2 decrease when the addition rate of ST is 3.0% compared to 0%. However, the use of ST may be necessary, as a previous study [6] found that depending on the type of FA, GP mortar may be hardened instantly if ST is not added. In the future, it will be further optimize the addition ratio of ST for different types of FA.

From the results of this experiment, a problem remained regarding the addition ratio of ST. However, regardless of the mixing method and the method of Na_2SiO_3 addition, when the FA had a specific surface area of approximately 7000 cm^2/g (i.e. FAII7 here), the DSP mixing ratio was up to 10.0%, and the concentration of Na_2SiO_3 aqueous solution is 3.0 mol/L, a maximum compressive strength of approximately 35 N/mm^2 is obtained at normal temperatures.

5. Conclusions

The following conclusions were obtained in this study:

1) For all four types of FA studied, the flow value, air content, and compressive strength of the GP are not affected by the addition method of Na_2SiO_3 and the mixing method.
2) When using an FA with a specific surface area of approximately 7000 cm^2/g, a DSP mixing ratio of 10.0%, and 3.0 mol/L Na_2SiO_3 aqueous solution, GP with the compressive strength of approximately 35 N/mm^2 is obtained at normal temperatures. However, the addition ratio of ST should be further investigated.

In the future, we intend to investigate in more detail the effects of the type of FA, mixing ratio of DSP, and the addition ratio of ST on the compressive strength and the reaction mechanism.

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