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CHARACTERISTICS OF STRENGTH AND FACTORS EFFECTING STRENGTH OF ALKALI-ACTIVATED SLAG CONCRETE

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Granulated blast furnace slag powder activated by some alkalies presents high hydraulic activity and can be used as a high strength alkali-activated cement (AS cement). However, because of different hydration mechanisms, the strength characteristics of AS cement differ from those of portland cement. In this paper, the strength characteristics of AS mortar and/or concrete and factors effecting on the strength such as hydraulic activity of the slag, fineness of slag, types and dosages of activators, curing temperatures, compatibility to other admixtures, W/C, are presented.

Key Words: *activator, admixture, alkali-activated slag cement, concrete, strength*

1. INTRODUCTION

The chemical composition of granulated blast furnace slag corresponds to melilite phase that is a solid solution phase between gehlenite ($2CaO \cdot Al_3O_2 \cdot SiO_2$) and akermanite ($CaO \cdot MgO \cdot 2SiO_2$). Gehlenite, akermanite and melilite are not reactive when crystalline [1). Even in non-crystalline state, the hydration of the blast furnace slag in pure water is very slow. So, some alkalies are required to activate the slag to reveal their hydraulic activity. Because some $Ca(OH)_2$ is released in the hydration of portland cement, the portland cement can be used as an activator for hydration of the blast furnace slag. As supplementary material, granulated blast furnace slag has been used in concrete for more than one hundred years. It can give some fine properties of long term strength, heat of hydration and durability to concrete. However, some of research reveal that the activity of the slag activated by sodium carbonate, sodium hydroxide or sodium silicate (soluble glass) are much higher than that activated by portland cement and this kind of alkali-activated slag cement (AS cement) and concrete (AS concrete) have very high strength and corrosion resistance [2)~7)]. This fact suggests that it is possible to use AS cement in place of portland cement to make high performance concrete. However, because blast furnace slag as a main composition of AS cement is a by-product, its hydraulic activity changes with the conditions of iron production. As a matter of course, it will influence the strength of AS concrete. Many factors such as hydraulic activity of slag, fineness of slag, types and dosages of activators and curing temperature all can control the strength of AS cement paste and AS concrete [8)~11)]. So, it is important to study the influence of the factors on the strength of hydrated AS cement paste and AS concrete.

Recently, various chemical and mineral admixtures have been used in concrete to improve the properties of the concrete. It is also expected to use these admixtures in AS concrete to modify the properties, especially workability and shrinkage of AS concrete. However, because the mechanisms of hydration and hardening of AS cement differ from those of portland, there is a problem of compatibility between the admixtures and AS cement. The compatibility between the admixtures and AS cement involves functions of the admixtures in AS concrete and influence of them on the strength. Therefore, it is necessary to study the effects of various admixtures on the strength of AS concrete.

Because some characteristics of strength of AS concrete such as evolution of strength and relationship between C/W and compressive strength have not been clear until now, it becomes one of the targets of this research to make clear these characteristics.

2. SCOPE OF THE INVESTIGATION

This paper aims to study the characteristics of strength of AS concrete and their influential factors. Therefore, first, effects of the main composition of AS cement, that is, blast furnace slag and activator, on strength of AS concrete have been investigated. One kind of ferro-chromium slag and three kinds of blast furnace slag that had different quality parameters (K_0 =CaO/SiO_2) were used to examine effect of hydraulic activity of slag on the strength. The influence of fineness of blast furnace slag on the strength of AS concrete was also investigated. In order to study the effects of activators on the strength of AS concrete, seven kinds of activator including sodium hydroxide, sodium sulfate, sodium carbonate and sodium silicates that had four different modulars (M =Na_2O/SiO_2) from 1 to 2.5 were used.

Second, the effects of curing temperatures on the strength of AS concrete were investigated.

Third, to research the compatibility between admixtures and AS cement, influence of the chemical admixtures (water reducer, super-plasticizers, and expansion producing admixtures) on the strength of AS concrete was investigated.

Finally, to investigate the characteristics and evolution of compressive strength of AS concrete, the relationship between cementitious material to water ratio (C/W) of AS concrete and the compressive strength of the concrete as well as the development of the strength with age of the AS concrete were researched.

Table 1 Chemical analyses of slags

Chemical Composition (wt%)	BFS1	BFS2	BFS3	FCS
CaO	43.43	42.54	36.77	2.92
SiO_2	32.19	38.30	35.33	32.84
Al_2O_3	13.73	12.75	10.02	18.16
Fe_2O_3	1.78	0.17	2.15	2.04
MgO	4.45	6.54	8.32	36.48
MnO	2.48	0.12	3.02	---
Basicity Requirement ($CaO+MgO+Al_2O_3$)/SiO_2	1.91	1.61	1.56	1.75
Quality Parameter K_0=CaO/SiO_2	1.35	1.11	1.04	0.09

3. TEST MATERIALS

(1) Slag

Four kinds of granulated slags as a main composition of AS cement were used in this research. One of them was granulated ferro-chromium slag (FCS) and the others were granulated iron blast furnace slag (BFS1 ~ BFS3). Their chemical analyses are shown in **Table 1**. From **Table 1**, it can be known that in the three kinds of blast furnace slag, two kinds (BFS1 and BFS2) conform to the basicity requirement of JIS A 6206, though all are in conformity with that JIS R 5211.

(2) Activator

Seven kinds of activators as another main composition of AS cement were used to activate slag in this research. They were sodium hydroxide, sodium carbonate, sodium sulfate and sodium silicates that had different modulars adjusted with sodium silicate (M=SiO_2/Na_2O= 3.2) and sodium hydroxide. The states and dosages of the activators are shown in **Table 2**.

(3) Fine Aggregate

Two kinds of sand were used as fine aggregate in this research. One of them was Chinese standard sand (F.M.=1.77) for making mortar specimens. Another was river sand (F.M.=2.69, specific gravity=2.63) for making concrete.

Table 2 States and dosages of activators

Activator	Molecular Formula	State	Dosage
Sodium Hydroxide	$NaOH$	Solid	3.8
Sodium Sulfate	Na_2SO_4	Solid	3.8
Sodium Silicate	$Na_2O \cdot SiO_2$	Liquid	3.8
	$Na_2O \cdot 1.7SiO_2$	Liquid	3.8
	$Na_2O \cdot 2.2SiO_2$	Liquid	3.8
	$Na_2O \cdot 2.5SiO_2$	Liquid	3.8
Sodium Carbonate	Na_2CO_3	Solid	3.8

Note: Dosage is Na_2O content/cementitious material.

Table 3 States and dosages of admixtures

Admixture Name	Type of Admixture	State	Dosage
Water reducer	Lignosulfonate	Liquid	0.33
Superplasticizer			
SP1	Sulfonated Naphthalene	Liquid	0.74
SP2	Sulfonated Naphthalene	Liquid	0.74
SP3	Sulfonated Naphthalene	Liquid	0.74
SP4	Sulfonated Naphthalene	Liquid	0.74
Expansion Prod-ucing Admixture	Calcium Sulfoaluminate	Solid	5
	Magnesium Oxide	Solid	5
	Calcium Oxide	Solid	5 ~ 10

Note: Dosage is a percentage of cemnetitious material.

(4) Coarse Aggregate

Crushed diabase was used as coarse aggregate in concrete. Its maximum size was 30 mm. Its specific gravity was 2.72.

(5) Admixture

Sodium lignosulfonate water reducer (WR), four kinds of sulfonated naphthalene formaldehyde superplasticizers (SP1 ~ SP4), and three types of expansion producing admixtures (calcium sulfo-aluminate type, magnesium oxide type and calcium oxide type) were used for researching the compatibility between the admixtures and AS concrete. The states and dosages of them are shown in **Table 3.**

4. EXPERIMENTAL WORKS

(1) Analysis of Hydraulic Activity of Slag

The hydraulic activity of slag was determined by two ways in this research. One was the quality parameter of slag ($K_0 = CaO/SiO_2$) that was deter-mined on chemical composition of slag. Another was heat of solution of slag that was determined according to JIS R 5203.

(2) Test of Compressive Strength of Hardened Mortar

All of the mortar specimens were made with a constant ratio of sand to cementitious material (S/C=2.50) and flow of the fresh mortar ranged from 117 to 134 mm. The specimens were compacted by a vibrating table. The specimens were cured in a fog curing room conditioned at 20 ± 2 ℃ and 95 ± 5 % R.H.. The specimens were 40 by 40 by 160 mm prisms. The test was performed according to GB 177-84 of China.

(3) Test of Compressive Strength of Hardened Concrete

Specimens of concrete were 150 by 150 by 150 mm cubes. The mixture proportions of the concrete are shown in **Table 4.** The specimens were cured at the same conditions as that of mortar specimens except the specimens for researching the influence of curing temperature on strength.

5. RESULTS AND DISCUSSION

(1) Influence of Compositions of AS Cement on Strength of Hardened AS Mortar

The main compositions of AS cement are ground slag and activator. So, the hydraulic activity and fineness of the slag as well as type and dosage of activators determine the strength of AS mortar and concrete directly.

a) Effect of hydraulic activity of slag on the strength

The intrinsic hydraulic activity of a slag depends upon various factors such as content of glass phase, chemical and mineralogical compositions. Slags having a higher content of glass phase are generally found to be more reactive. But it is of intricacy to measure the content of glass phase in slag. Sometimes, heat of solution of slag dissolved

Table 4 Mixture proportions of AS concrete

Test	W/C (%)	s/a (%)	Water (kg/m³)	Cement (kg/m³)	Slump (cm)
Curing Temperature	38	32	189	501	20
Long-term Strength	35	30	160	457	9
Relation of C/W and strength (sodium silicate type activator)	35 40 45 50 55 60	30 36 37 38 39 40	160 160 160 160 163 169	457 400 355 320 296 282	9 9 8 8 8 8
Relation of C/W and strength (sodium sulfate type activator)	35 40 45 50 55 60	30 36 37 38 39 40	156 156 156 156 160 165	445 390 347 312 290 275	9 9 9 8 8 8

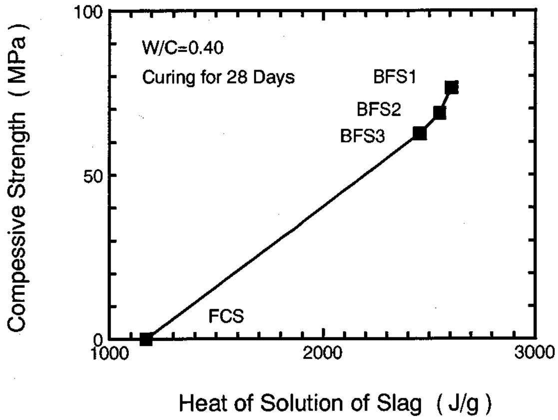

Fig.1 Relation between heat of solution of slag and compressive strength of AS mortar

in a solution of nitro-hydrofluoric acid may be used for measuring content of glass phase in slag indirectly [12]. In this paper, this method was used also. The heat of solution of a granulated ferro-chromium slag and three kinds of granulated blast furnace slags was measured respectively. At the same time, the compressive strengths of hardened mortar specimens made with respective slags and the same activator ($Na_2O \cdot SiO_2$) were determined, too. The relationship between heat of solution of slag and compressive strength of its mortar specimens is given in **Fig.1**. From **Fig.1**, it can be found that the compressive strength of AS mortar specimen increases with the increase of the heat of solution of the slag used for making the AS mortar. That is, the strength of AS mortar increases with the content of glass phase in slag.

Because slag is mainly composed of a silicate network neutralized by cations such us calcium, magnesium, or aluminium, there may be a relationship between hydraulic activity of slag and its chemical compositions. Although various modules have been proposed to express the relationship between the hydraulic activity and the chemical compositions, e.g., CaO/SiO_2, $(CaO+MgO)/SiO_2$, $(CaO+Al_2O_3+MgO)/SiO_2$, $(CaO+MgO)/(SiO_2+Al_2O_3)$, CaO/SiO_2 called quality parameter K_0 was only used to evaluate the hydraulic activity of slag because the magnesium composition of slag was not beneficial to hydraulic activity in the hydration of AS cement. It is, therefore, difficult to apply the JIS basicity requirement to AS cement. The relationship between quality parameter of slag and compressive strength of the AS mortar specimens is shown in **Fig.2**. From this figure, it is clear that compressive strength of the AS mortar increases with increase of quality parameter of slag.

b) Effect of fineness of slag on the strength

Although it has been known that hydraulic activity of slag in portland cement can be controlled by changing the fineness of the slag ground [1], it is not clear in AS cement. In **Fig.3**, it can be seen that the AS mortar specimens made with finer slag powder had higher compressive strength. Especially, the AS mortar specimens made with finer slag powder had much higher early strength. This fact evidences that grinding slag more finely makes the powder have higher hydraulic reactivity in AS cement.

c) Effect of types of activator on the strength

The type of activator gives very strong influence on the strength of the AS mortar or AS concrete. **Fig.4** shows that AS mortar specimens made with different types of activator but the same admixture dosage of alkali had much different compressive strength. Although pH of the solution of activator of NaOH was the highest in all of the activators in this research, the compressive

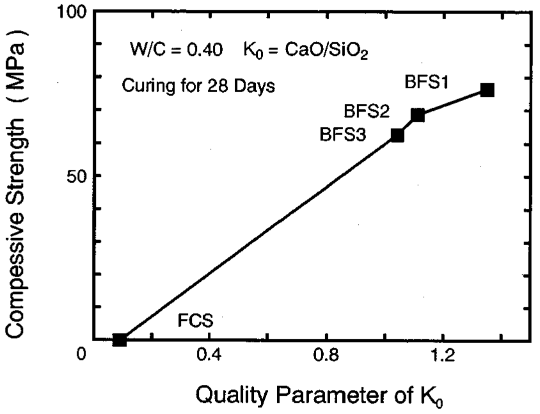

Fig.2 Relation between quality parameter of slag and compressive strength of AS mortar

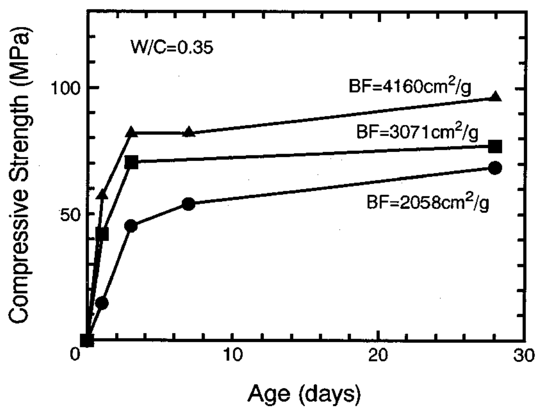

Fig.3 Effect of fineness of slag on compressive strength of AS mortar

strength of the AS mortar specimen activated by it was the lowest in the all specimens. It seems that the strength of AS mortar depends not only on the activating effect of activator on slag but also on kinds of hydrate resulted from the reaction between activator and slag. So, according to this opinion the anions of activator play a very important action in strength of AS mortar or AS concrete. It is believed that activator of sodium silicate makes AS mortar have the highest strength because the anions of silicate can react with slag to form some hydrates of silicate that have high strength.

Further, although the AS mortar specimens were made by addition of the same type of activators of sodium silicate, they had different strength with their different modules. It can be found easily from the definition of module that the molar ratio of silica increases with the module but pH of its solution decreases. This suggests that there is an optimum module in which the activator gives slag such better activation and hydrates that it makes AS mortar or AS concrete have the highest strength.

d) Effect of dosage of activator on the strength

Generally, activation of activator also depends on the dosage of the activator, that is, it increases with the dosage of the activator. So, dosage of activator can also control the strength of AS mortar and evolution of strength of AS mortar. The compressive strengths of AS mortar specimens with the same activator ($Na_2O \cdot SiO_2$) but

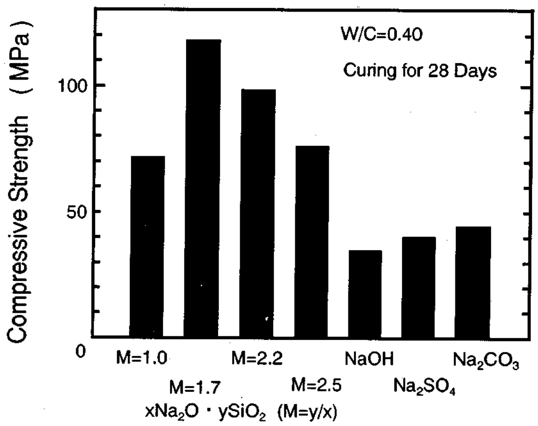

Fig.4 Compressive strength of AS mortar with different type of activators

different dosages are shown in **Fig.5**. The compressive strength of the AS mortar specimens added by higher dosage of the activator had higher compressive strength especially in early strength.

(2) Influence of Curing Temperatures on Strength of AS Concrete

The strength of AS concrete is more sensitive to the curing temperatures, because the heat of hydration of AS cement is much lower than that of portland cement, which is only about half of that of portland cement for 7 days [7]. The effect of

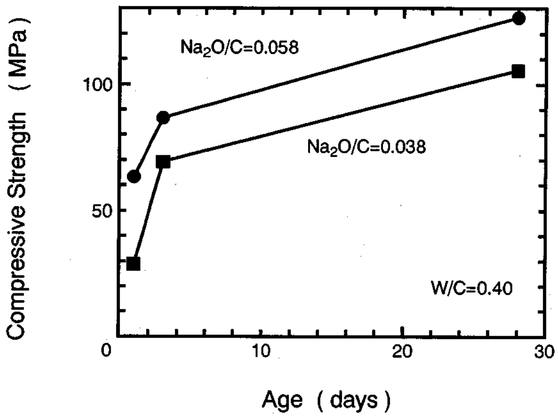

Fig.5 Compressive strength of AS mortar with different dosages of activator

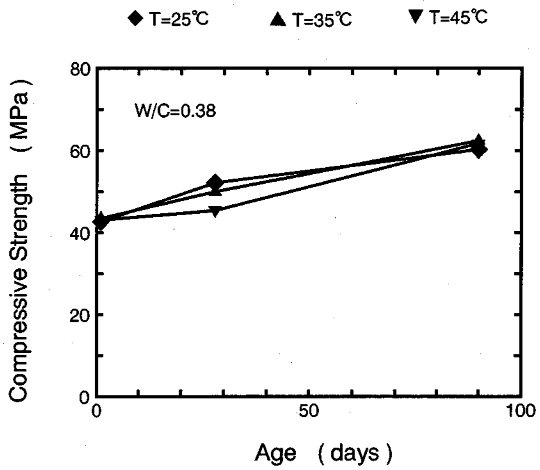

Fig.7 Effect of curing temperature on long–term compressive strength of AS concrete

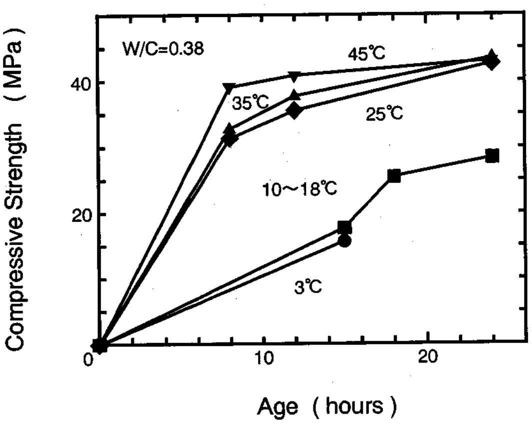

Fig.6 Effect of curing temperature on early compressive strength of AS concrete

curing temperatures on compressive strength of AS concrete in the first 24 hours is shown in **Fig.6.** The mixtures of concrete is shown in **Table 4.** Although the specimens in this test had the same mixture proportion, the compressive strengths of the specimens were much different from each other. The early compressive strength of AS concrete increased with raise of the curing temperature and especially the compressive strength of the AS concrete increased faster in the range from 10 to 25 ℃ . The curing temperature above 10 ℃ seams to be necessary for AS concrete to get higher strength at early age. However, the raise of curing temperature from 25 ℃ to 45 ℃ had not so much effect as it in the range from 10 to 25 ℃ on the compressive strength of AS concrete. The effect of early curing temperatures on the long–term compressive strength of the concrete is given in **Fig.7.** The specimens of AS concrete were cured at different temperatures only in the first day and then they all were cured at 20 ℃ . From **Fig.7**, it can be seen that the early curing temperature had little effect on long–term compressive strength of AS concrete.

(3) Influence of Admixtures on Strength of Hardened AS Mortar

In order to solve problems on the compatibility between chemical admixtures and AS concrete because of different mechanisms of hydration and hardening of AS cement, the effects of the admixtures on strength of AS mortar and concrete have been approached.

a) Effect of water reducer on the strength

Flow of fresh AS mortar containing sodium lignosulfonate water reducer is shown in **Fig.8** and effect of the water reducer on compressive strength of AS mortar is shown in **Fig.9**. From this figure, it can be found that sodium lignosulfonate had an intensely negative effect on the early compressive strength of AS mortar but little effect on the long–term compressive strength of AS mortar. The effect of sodium lignosulfate on the early strength of AS mortar may connect with its retarding action on hydration of AS cement.

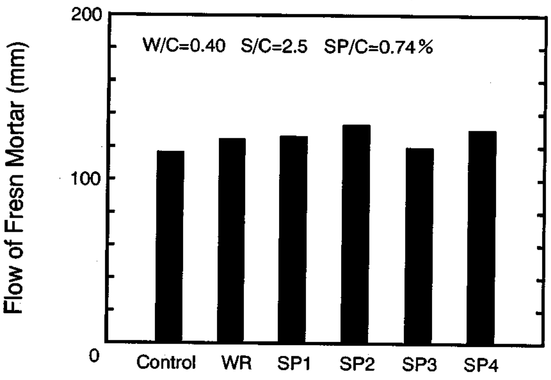

Fig.8 Flow of fresh AS mortar containing water reducer or superplasticizers

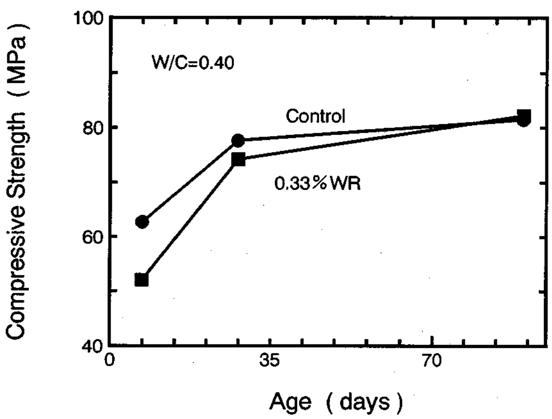

Fig.9 Effect of water reducer on compressive strength of AS mortar

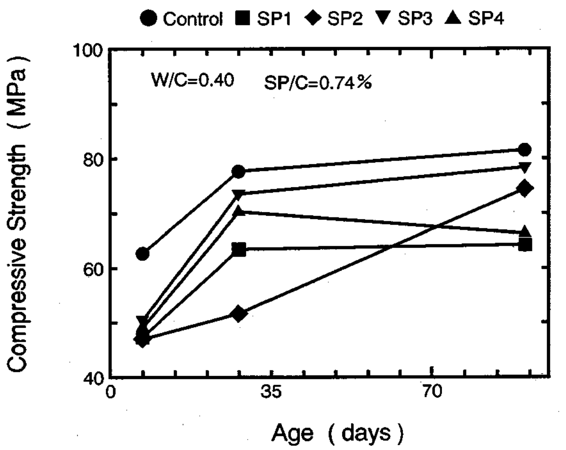

Fig.10 Effect of superplasticizers on compressive strength of AS mortar

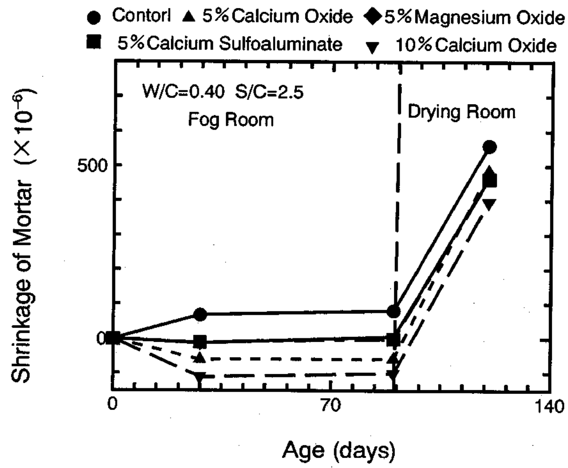

Fig.11 Shrinkage of AS mortar containing expansion producing admixtures

b) Effect of superplasticizers on the strength

Flow of fresh AS mortar containing sulfonated naphthalene formaldehyde superplasticizer (SP1 ~ SP4) is also shown in **Fig.8**, and effect of the superplasticizers on compressive strength of AS mortar is given in **Fig.10**. It is shown that all the superplasticizers in this test reduced the early compressive strength of the AS mortar to the same degree but the effect of the superplasticizers on long-term compressive strength was very different. Although the type of the superplasticizers was the same, the makers were different. So, some factors, e.g., raw materials, procedure of production, and condensation of the superplasticizers, may determine the effect of the superplasticizers on the compressive strength of AS mortar.

c) Effect of expansion producing admixtures on the strength

The shrinkage of mortar containing calcium sulfoaluminate, calcium oxide and magnesium oxide expansion producing admixtures respectively is shown in **Fig.11**. Effect of them on the flexural strength of AS mortar is shown in **Fig.12**. From the two figures, it is clear that all the expansion

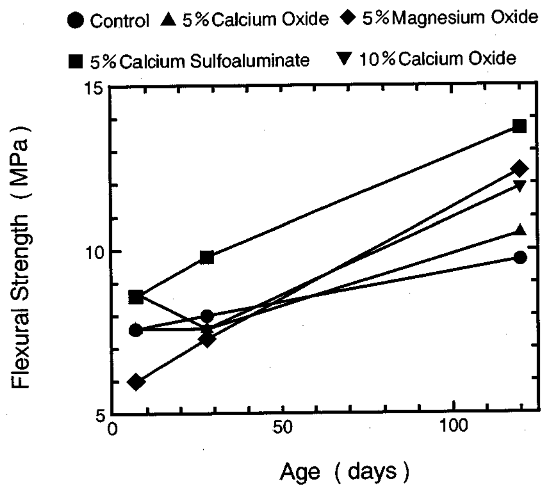

Fig.12 Effect of expansion producing admixtures on flexural strength of AS mortar

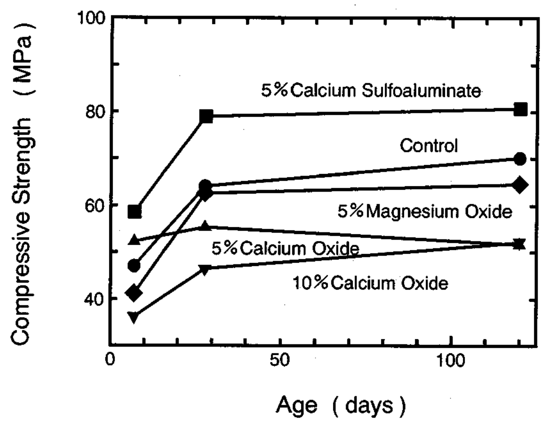

Fig.13 Effect of expansion producing admixtures on compressive strength of AS mortar

producing admixtures could increase the flexural strength of AS mortar because they could reduce a part of shrinkage of AS mortar that may cause some cracks in the mortar to decrease the flexural strength. The effect of the expansion producing admixtures on compressive strength of AS mortar is given in **Fig.13**. The addition of calcium sulfoaluminate could increase the strength, and the addition of magnesium oxide decreased the compressive strength a litter, but the addition of calcium oxide decreased the strength obviously. The different influence may connect with the reactions between the activator and expansion producing admixture.

(4) Relationship between C/W and Compressive Strength of AS Concrete

In portland cement concrete, the compressive strength of the concrete is controlled by the cement to water ratio (C/W) of the concrete and hydration degree of the cement in the concrete according to the theory of gel/space ratio [13] . The theory of gel/space ratio may also suit to AS concrete since the main hydrate of AS cement is low C/S CSH gel [2] . However, it has been discussed in above section (1) that the compressive strength of AS mortar depends on the hydration of AS cement and the hydration is controlled by not only slag powder and also activator. Therefore, when the theory of gel/space is used in AS concrete, the factor of activator should be considered.

Relation between C/W and compressive strength of AS concrete whose mixture proportions are given in **Table 4** is shown in **Fig.14**. From this figure, it can be known that there is a linear relation between C/W and compressive strength for a given AS concrete. From the same figure, it is also known that type of activator can influence the relation as the activators have different effects on the hydration of AS cement.

(5) Evolution of Strength of AS Mortar and AS Concrete

Some types of cement that have higher early strength have a problem about decrease of long-term strength. It is also concerned with AS cement. Evolution of strength of AS mortar and concrete whose mixture proportions are shown in **Table 4** with the age is given in **Fig.15**. From the figure, it can be concluded that there is not any problem about long-term strength of AS cement. The strength of AS concrete increases with the age for a very long time. So, it is one of excellent properties of AS cement.

6. CONCLUSIONS

In this paper, the characteristics of strength of AS concrete have been studied and some conclusions are obtained as follows:

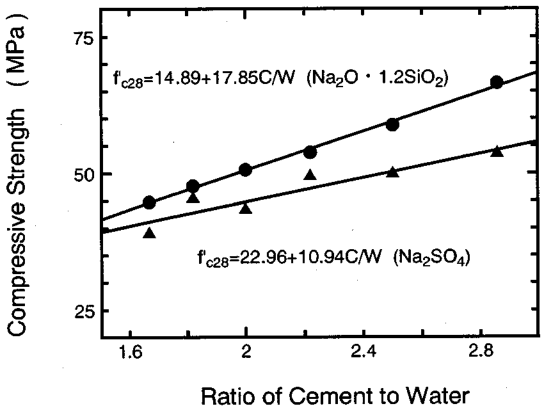

Fig.14 Relation between C/W and compressive strength of AS concrete

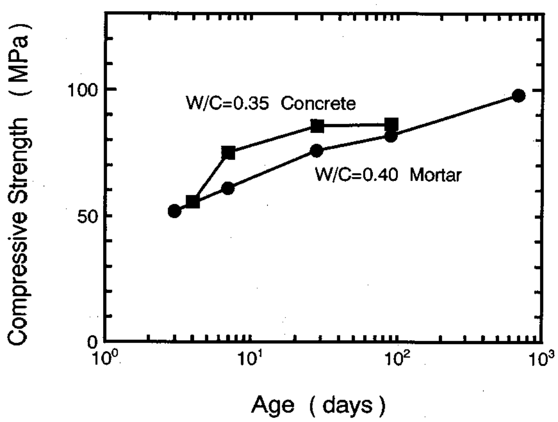

Fig.15 Evolution of compressive strength of AS concrete

(1) Slag and activator as the main compositions of AS cement determine the strength of hydrated AS cement. The AS cement made by the slag that has higher quality parameter and heat of solution may have a higher strength after hydration. The higher fineness of slag is, the higher is the strength of the hydrated AS cement. The strength of hydrated AS cement also depends on the type and dosage of activator. Sodium silicate gives hydrated AS cement the highest strength in the all activators in this research. The strength of hydrated AS cement increased with the increase of dosage of activator.

(2) The compressive strength of AS mortar and concrete increases with curing temperature especially at early ages. The curing temperature above 10 ℃ is necessary for AS concrete when higher early strength is required.

(3) Because water reducer and superplasticizers may retard hydration of AS cement, they decrease early strength of AS concrete but effect of them on long-term strength of AS concrete is very different. Expansion producing admixtures can increase flexural strength of AS concrete as they can reduce the cracks produced with the shrinkage of the paste. However, they may increase or decrease the compressive strength of AS concrete according to types of them.

(4) The compressive strength of AS concrete is directly proportional to C/W of the concrete, and the relation between compressive strength and C/W of AS concrete is also controlled by activator intensely.

(5) AS concrete has very high compressive strength in early ages and the compressive strength increases with the age of the concrete for very long time.

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アルカリースラグコンクリートの強度特性と影響を及ぼす因子

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高炉スラグ微粉末をアルカリで刺激することにより，高強度セメントとして用いることが可能である．しかし，高炉スラグ微粉末をアルカリで刺激してセメントとして用いた場合の強度特性は普通ポルトランドセメントの強度特性と異なり，強度に及ぼす影響の因子や，強度と材齢の関係など明らかにされていない点が多い．本文は，アルカリースラグモルタルとコンクリートの強度特性並びに，強度に影響を及ぼす因子（スラグの水和活性と粉末度，アルカリ刺激剤の種類と添加量，養生温度，混和剤，水セメント比など）の作用を検討したものである．