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INFLUENCE OF MICROSTRUCTURE ON THE PHYSICAL PROPERTIES OF CONCRETE PREPARED BY SUBSTITUTING MINERAL POWDER FOR PART OF FINE AGGREGATE

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ABSTRACT

The hydration reaction of cement, hardened structure and pore structure in concrete prepared by substituting a large quantity of mineral powder including fly ash, slag, limestone and silicious stone for part of fine aggregate in concrete have been studied and the relationships between the substitution of those mineral powders and the physical properties of concrete have been investigated. Increase in viscosity and decrease in fluidity of concrete by the substitution of the mineral powder for part of fine aggregate are mainly caused by the increase of fine particles non-existent in fine aggregate. Higher strength than that of concrete without substitution in the case with the same slump is brought by the densification of hardened concrete structure by filling effect of mineral powder itself and, in some cases, of C-S-H produced by pozzolanic reaction. The slight increase of creep of the concrete prepared by substituting fly ash for part of fine aggregate may be caused by offsetting the increase of the practical quantity of cement paste in concrete by the improvement of strength of the hardened concrete. The reduction of dynamic Young's modulus may be caused by the increase of practical quantity of cement paste with the dynamic Young's modulus almost half that of aggregate.

Introduction

A research has been made for blending a large quantity of a mineral powder with concrete as an alternative to portland cement for the reduction of the environmental load, preservation of resources and improvement of performance. The development of high volume fly ash concrete (HVFC) by CANMET (1) is an example of the development. Large quantities of particle-size adjusted-reactive mineral powders including quartz powder have recently been used for obtaining the closest packing for reactive powder concrete (RPC) (2) gaining attention as an ultra-high strength material.

Also in Japan, cement prepared by substituting a large quantity of particle-size adjusted limestone powder for a considerably large part of portland cement is used for high-fluidity concrete and some studies for substituting fly ash for part of fine aggregate in concrete (3,4) are

TABLE 1

Chemical Composition, Specific Gravity and Adsorbed Quantity of Chemical Admixture of Various Mineral Powders

Kind of mineral powders used to substitute for fine aggregate	Chemical composition (%)								Specific gravity	Adsorbed quantity of chemical admixture (mg/g)
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O		
Fly ash	50.0	37.4	5.8	1.5	0.7	0.3	0.4	0.5	2.32	3.3
Limestone powder	34.2	16.1	0.3	41.0	6.4	0.4	0.1	0.2	2.89	1.0
Blast furnace slag powder	0.5	0.4	0.1	55.0	0.4	0.0	0.1	0.1	2.70	0.7
Silicious stone powder	97.5	0.8	0.2	0.1	0.0	0.0	0.0	0.0	2.64	1.4
Portland cement	21.6	5.3	3.3	64.9	1.1	2.3	0.45	0.35	3.15	2.3

being made. The mineral powder has a tendency not only to be used as a blending component to cement but to be used directly and in large quantities as a raw material for preparing concrete. Since the change of the physical properties of concrete by increasing the mineral powder used as an blending component to cement are on an extension of those of concrete prepared by using blended cement, the change of physical properties can be easily estimated. This is, therefore, not a practically important problem. The physical properties of concrete are, however, remarkably changed by substituting the mineral powder for part of fine aggregate. For instance, the fluidity of fresh concrete is decreased and plastic viscosity is increased by substituting fly ash for part of fine aggregate, thereby increasing the requirements of a chemical admixture. And the deflection of hardened concrete is increased because the creep is slightly increased and the dynamic Young's modulus is approximately 10% decreased (5).

This study has been made by analyzing the hydration reaction of cement, hardened structure and pore structure of concrete and determining the relationship between those items and the physical properties of concrete keeping the unit quantities of water and cement constant, aiming at clearing up the cause of the change of the physical properties of concrete by substituting the mineral powder including fly ash, slag, limestone and silicious stone for part of fine aggregate.

Experimental

Samples and Preparation of Test Specimens. The compositions and specific gravities of ordinary portland cement, fly ash, slag, silicious stone and limestone powders and the adsorbed quantities of chemical admixtures used for the experiment to them are listed in Table 1. The fineness of those materials are adjusted to 3,500 cm^2/g of Blaine's specific surface area. The unit quantities of cement and water for the concrete mix are 300 and 176 kg/m^3, respectively, as shown in Table 2. Each mineral powder is used so as to make the unit volume of all the powders including cement 200 l/m^3. A run of experiment using 75 kg of fly ash/m^3 corresponding to 1/4 of the quantity of cement was added. The quantities of fine and coarse aggregates are constant in every mix. In the experiment using 75 kg of fly ash/m^3 (F75), the quantity of coarse aggregate is the same as in the other runs of experiment and the fine aggregate is adjusted to 669 kg/m^3. Land sand from Ogasa and crushed stone from Iwase are used as the fine and coarse aggregates, respectively. A polycarboxylic acid-based high-performance AE water reducing agent and an AE agent are used as the chemical admixture.

The target slump and volume of air are 18.0 cm and 4.0%, respectively. The dimensions of

TABLE 2

Mix Proportion of Concrete

Kind of mineral powders used to substitute for fine aggregate	Symbol	Unit quantity (kg/m³) Water	Portland cement	Mineral powder	Fine aggregate	Coarse aggregate	Super-plasticizer	Water/ Powder*	Slump (cm)	Air (%)
Plain	P	176	300	0	754	1024	—	0.59	16.5	4.3
Fly ash	F	176	300	227	495	1024	5.53	0.33	17.5	4.0
Fly ash	F75	176	300	75	669	1024	0.75	0.47	16.0	6.0
Blast furnace slag powder	S	176	300	304	495	1024	4.23	0.29	15.0	3.2
Limestone powder	C	176	300	284	495	1024	3.50	0.30	20.0	4.9
Silicious stone powder	Q	176	300	277	495	1024	4.62	0.31	19.5	4.9

* Powder : Portland cement + Mineral powder

the test specimens are 10 cm in diameter and 20 cm high. The test specimen is released from the mold 24 hours after placing and cured in water at 20°C till a specified age.

Experimental Method. The measurement of slump and the strength test of it are conducted according to JIS A 1101 and A 1108, respectively. The sample for each measurement is prepared by cutting a test specimen of hardened concrete into approximately 5 mm cube, immersing it in acetone to terminate the hydration. And then it is D-dried. The volume of capillary pore is measured by the mercury-intrusion method (6). The structure of hardened concrete is observed by the back scattered electron image and the distribution of elements including Ca and Al in hardened concrete is determined by secondary x-ray analysis with a computer-aided electron probe microanalyzer (CMA/EPMA). The structure of fracture surface of hardened concrete is observed by FESEM. The combined water and $Ca(OH)_2$ are determined by the ignition loss method at 1000°C and the thermogravimetry (TG) -differential scanning calorimetry (DSC) (7), respectively. The adsorbed quantities of the high-performance AE water reducing agent to the mineral powder are measured by the method described in the previous paper (8).

Experimental Results

Slump and Compressive Strength of Concrete. The values of slump and compressive strength of concrete prepared by substituting the mineral powders for part of fine aggregate are listed in Table 2 and illustrated in Fig. 1. The quantity of the high-performance AE water reducing agent required for obtaining specified slump is increased by the substitution. The increase of the chemical admixture varies according to the kind of mineral powder. Fly ash requires approximately 1.5 times as much chemical admixture as limestone powder. The more the adsorbed quantities of admixture, the larger the requirements of it are, as reported in the previous paper (8). It is estimated that the increase of the viscosity and the decrease of fluidity of fresh concrete by substituting the mineral powder for part of fine aggregate are caused by the increase of fine particles non-existent in the fine aggregate. The fluidity of concrete prepared by the substitution of fly ash is lower than using limestone powder. This suggests that the effects of the shape of mineral powder on the viscosity and fluidity of fresh concrete are not so large.

The development of strength of concrete caused by substituting the mineral powder for part of fine aggregate is illustrated in Fig. 1. The strengths of plain concrete—10.6 MPa at the age of 3 days, 17.0 MPa at the age of 7 days, 26.8 MPa at the age of 28 days and 32.4 MPa at the

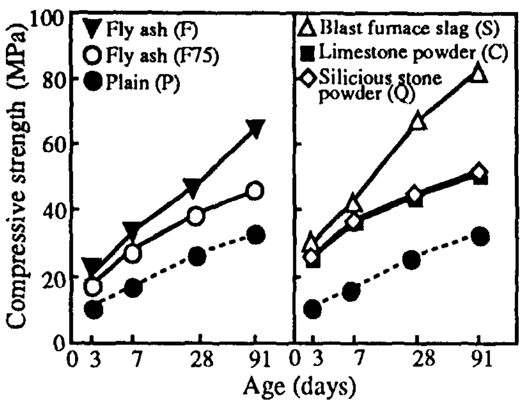


FIG. 1.
Compressive strength of concrete prepared by substituting the mineral powders for part of fine aggregate.

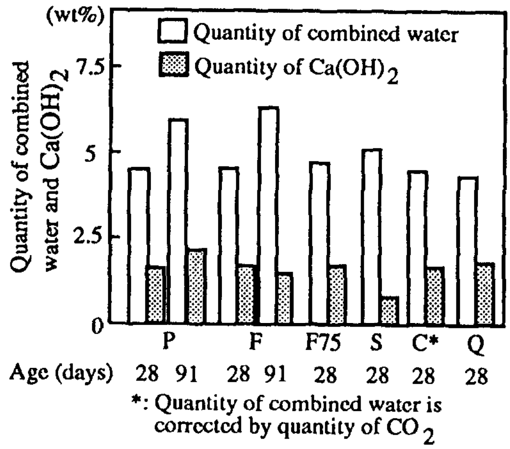


FIG. 2.
Content of combined water and $Ca(OH)_2$ in concrete prepared by substituting the mineral powders for part of fine aggregate.

age of 91 days—are lower than those of concretes prepared by substituting the mineral powders for part of fine aggregate and the differences generally increase with the increase of the age. The compressive strength of concrete prepared by substituting slag powder for part of fine aggregate are as large as 67.6 and 80.0 MPa at the ages of 28 and 91 days, respectively. The contents of $Ca(OH)_2$ and combined water in hardened concrete illustrated in Fig. 2 and the back scattered electron images illustrated in Fig. 3 reveal that the increase of strength by substituting the mineral powder may be caused by the decrease of the practical W/C ratio [water/whole powders (cement + mineral powder)] and the progress of pozzolanic reaction of slag powder added for substitution with $Ca(OH)_2$. The strengths of concrete prepared by substituting limestone and silicious stone powders for part of fine aggregate are higher at the ages of 3 and 7 days than those of concrete prepared by the substitution of fly ash. It is inferred from the content of $Ca(OH)_2$ in hardened concrete shown in Fig. 2 and the segmental pore size distribution in hardened concrete shown in Fig. 5 that the porosity is reduced because the large pores in concrete are filled with those mineral powders. Fig. 2 and Fig. 5 suggest that the increase of the strength of concrete prepared by substituting fly ash for part of fine aggregate from the age of 28 days on is caused by the densification of the structure by C-S-H produced in the pozzolanic reaction.

Contents of Combined Water and $Ca(OH)_2$ in Concrete. The contents of combined water and $Ca(OH)_2$ in concrete prepared by substituting the mineral powder for part of fine aggregate are illustrated in Fig. 2. In the concrete prepared by substituting slag for part of fine aggregate, the content of combined water at the age of 28 days is the highest and that of $Ca(OH)_2$ is the lowest. This suggests that the pozzolanic reaction proceeding in the concrete produces C-S-H. The contents of combined water and $Ca(OH)_2$ in the concretes prepared by substituting limestone and silicious stone powders for part of fine aggregate are almost equal to those in plain concrete. It is inferred from this that the pozzolanic reaction hardly proceeds in them. In the concrete prepared by the substitution of fly ash, the content of combined water is higher while that of $Ca(OH)_2$ is lower at the age of 91 days than those in plain concrete. This suggests that the pozzolanic reaction proceeds in it.

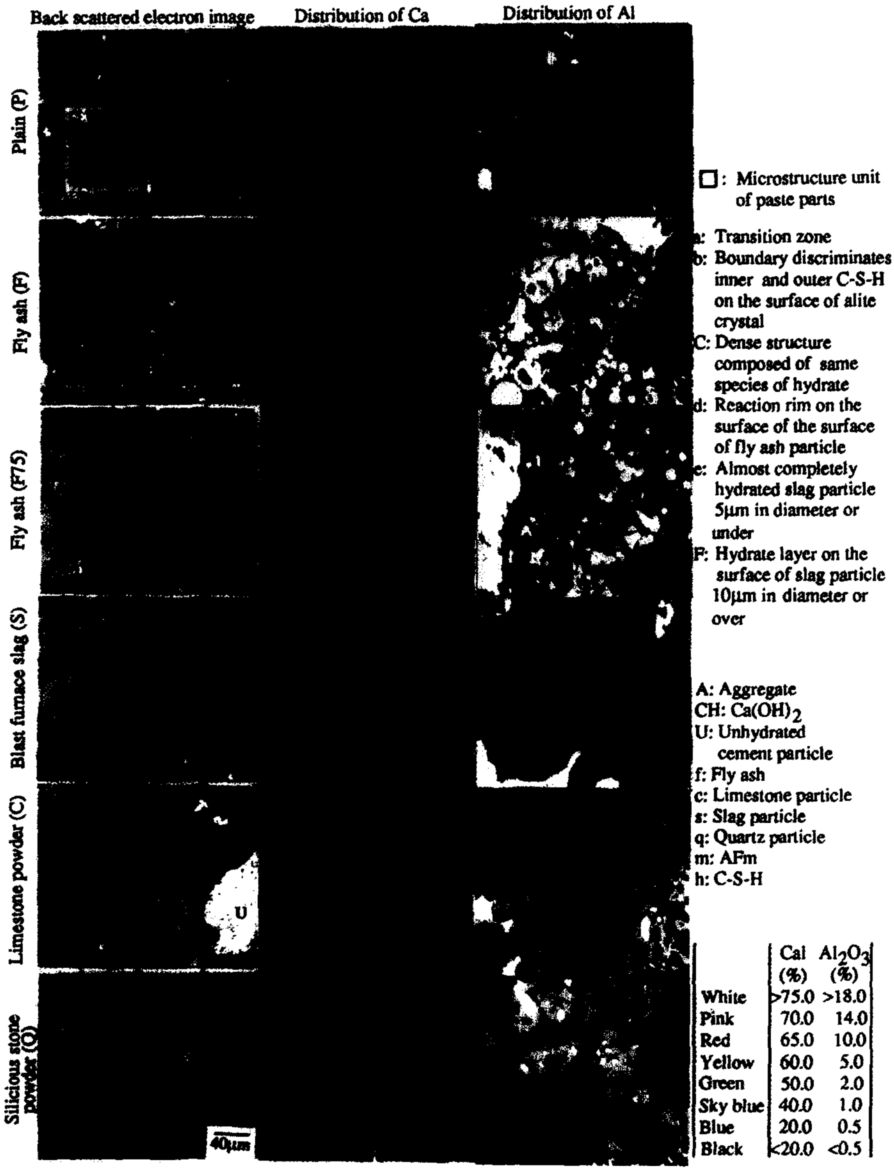
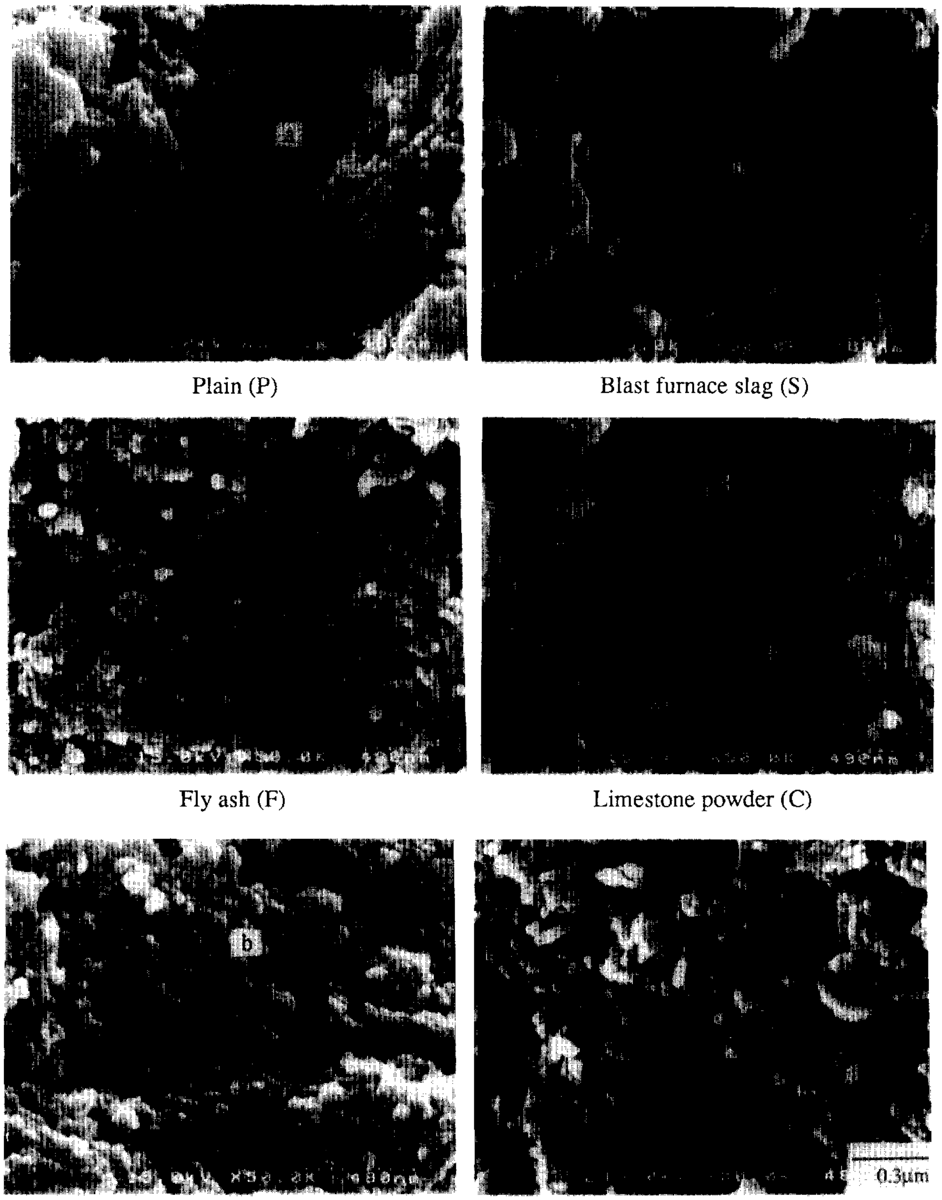


FIG. 3.
Back scattered electron image and distribution of Ca and Al on the polished surface of concrete prepared by substituting the mineral powders for part of fine aggregate (91 days).

<u>Structure of Hardened Concrete.</u> The back scattered electron images and the distributions of Ca and Al on the polished surface of the concretes prepared by substituting the mineral powders are illustrated in Fig. 3.

The hydration products of cement and some unhydrated cement particles are distributed over the matrix part in plain hardened concrete. The transition zones are formed around the aggregate by the deposition of $Ca(OH)_2$ (9) produced in the hydration reaction of cement.



Plain (P) | Blast furnace slag (S)
Fly ash (F) | Limestone powder (C)
Fly ash (F75) | Silicious stone powder (Q)

FIG. 4.
Secondary electron image of fracture surface of concrete prepared by substituting the mineral powders for part of fine aggregate (91 days): (a) large sized C-S-H with about 0.2 μm in diameter; (b) small sized C-S-H with about 0.1 μm in diameter.

Large-sized monosulfate hydrate (AFm) crystals are deposited in porous parts of the matrix while C-S-H is produced around the unhydrated alite. The boundary between the inner and outer C-S-H is relatively clear. The repetitive unit size of the hydrated structure is as large as approximately 200 μm.

In the concrete prepared by substituting the mineral powder for part of fine aggregate, the free water occupied-space ready for the deposition of hydration products which is formed in the setting and hardening process in plain concrete is filled with the mineral powder in advance, hence the space is smaller than that in plain concrete. Consequently, the quantity as well as the size of the hydrate produced is reduced. The deposition of $Ca(OH)_2$ around the aggregate is remarkably reduced by the inhibition of movement of pore solution to the aggregate accompanied with the decrease of the practical W/C ratio and by the consumption of $Ca(OH)_2$ in the pozzolanic reaction.

In the concrete prepared by substituting fly ash for part of fine aggregate, a dense structure composed of the hydration product of the same species is observed. It is confirmed from the distribution of Ca determined at the age of 91 days that the fly ash has a reaction rim on the surface of particle.

The structure of hardened concrete prepared by low substitution rate of fly ash (F75) is about the same as that of plain concrete except that fly ash particles are scattered in the matrix.

In the concrete prepared by substituting slag powder for part of fine aggregate, the slag particles are so well dispersed in cement paste that the fine particles 5 μm in diameter or under are almost completely hydrated showing a dark color at the age of 91 days and the hydrate layer is observed around the particles of 10 μm in diameter or over. The rate of the pozzolanic reaction is higher in the particles existing closer to the aggregate.

In the concretes prepared by substituting limestone and silicious stone powders for part of fine aggregate, these particles are almost evenly distributed over the matrix part. The size of the dense structure mentioned before is smaller than that in the concrete prepared by the substitution of fly ash. The limestone and silicious stone powders have a sharply edged shape and a wedge shape, respectively. Both powders show no pozzolanic reaction.

The secondary electron images of the fracture surface of hardened concrete taken by FESEM at the age of 91 days are illustrated in Fig. 4. The C-S-H hydrate has equi-dimensional shape and the particle diameter is approximately 0.2 μm in plain concrete, while those in the concretes prepared by substituting the mineral powder for part of fine aggregate are smaller than that regardless of the kind of mineral powder, particularly those in the concretes using slag and fly ash are as small as approximately 0.1 μm, and it has a dense structure composed of crowded C-S-H. The reduced size of hydrate is considered to be mainly caused by the decrease of practical W/C ratio and partly caused by the production of smaller C-S-H in the pozzolanic reaction than C-S-H directly produced by the hydration of clinker minerals.

Pore Structure of Hardened Concrete. The pore size distributions of the hardened concrete prepared by substituting the mineral powders for part of fine aggregate are illustrated in Fig. 5. It is considered that the pores except air void in the hardened concrete include the pore 6 nm or under in diameter corresponding to gel pore mainly exists in precipitated C-S-H structure, that 6 to 50 nm in diameter corresponding to capillary pore formed in hydrates and that 50 nm or over in diameter corresponding to large diameter capillary pore mainly forming a transition zone (9). Thus classified pore size distribution is illustrated in Fig. 6.

In the concrete prepared by substituting slag for part of fine aggregate, the volume of capillary pores of 50 nm or over is extremely smaller and gel pore of 6 nm or under is larger than in plain concrete. Accordingly, the total pore volume is remarkably smaller than in plain concrete. This is because the gel pore is formed by filling up the large diameter capillary pores with fine C-S-H produced by the pozzolanic reaction of slag.

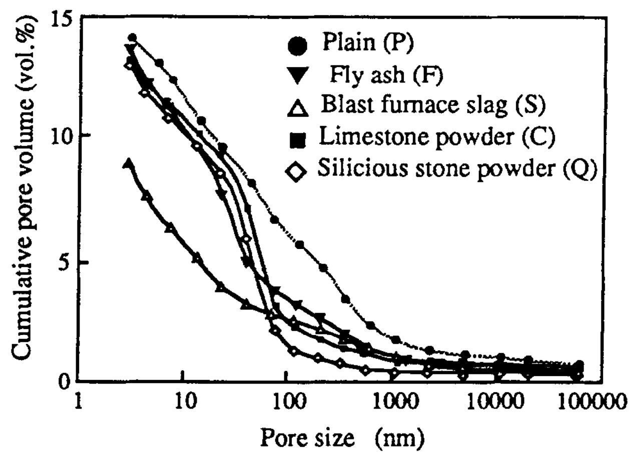


FIG. 5.
Cumulative pore volume of concrete prepared by substituting the mineral powders for part of fine aggregate (28 days).

In the concretes prepared by substituting fly ash and limestone and silicious stone powders for part of fine aggregate, the total pore volume of 14% is nearly equal to that in plain concrete, but the pore ratios by diameter to the total pore volume are different from each other in such a way that the volume of large diameter pore of 100 nm or over is smaller and those of capillary pores of 6 to 50 nm and gel pores of 6 nm or under are larger than in plain concrete. Maybe this is because fly ash and limestone and silicious stone powders densifies the structure of fresh concrete followed by that of hardened concrete by the filling effect of them, thereby inhibiting the movement of pore solution, the deposition of large crystal of $Ca(OH)_2$ and the formation of transition zone. The proceeding of pozzolanic reaction contributes to the densification of concrete structure from the age of 28 days on in the concrete prepared by substituting fly ash for part of fine aggregate.

It is concluded from the results mentioned above that the hydration reaction, hydration products and hardened structure of the concretes prepared by substituting the mineral powders for part of fine aggregate are not substantially different from those of concrete prepared by using fly ash cement, blast-furnace slag cement and inert mineral powder blended cement with high content of blending components except for the densification of hardened structure by the filling effect of mineral powder itself.

<u>Other Physical Properties of Hardened Concrete.</u> It is already known that the strength of concrete closely correlates with the volume of capillary pore of 50 nm or over mainly caused by the transition zone (9) The relationships in the concretes prepared by substituting various mineral powders for part of fine aggregate at various ages between the volume of capillary pore of 50 nm or over and the compressive strength are illustrated in Fig. 7. The strength corresponds to the volume of capillary pore regardless of the kind of the mineral powder and age of concrete. This is because the strength of concrete is developed by filling up the porous structures including the transition zone existing in the concrete with the mineral powder itself or C-S-H produced by the pozzolanic reaction.

The creep is slightly increased and the dynamic Young's modulus is decreased by approximately 10% in the concrete prepared by substituting fly ash for part of fine aggregate. The reason of the increase of creep is considered as follows: It may be regarded that a part of

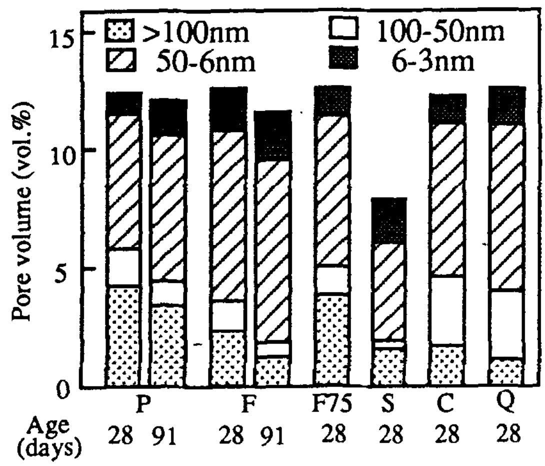


FIG. 6
Classified pore size distribution of concrete prepared by substituting the mineral powders for part of fine aggregate.

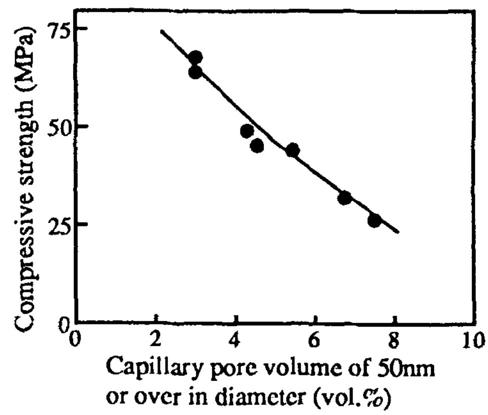


FIG. 7.
Relationship between capillary pore volume of 50 nm or over in diameter and compressive strength of concrete prepared by substituting the mineral powders for part of fine aggregate.

space occupied by fine aggregate is replaced with fly ash cement paste in the concrete prepared by substituting fly ash for part of fine aggregate, therefore the practical quantity of cement paste [quantity of cement paste estimated from the quantity of both portland cement and substituting mineral powder for part of fine aggregate] in unit volume of concrete is substantially increased, and the distance between the pieces of aggregate is increased. Meanwhile the volume of pore in concrete is not changed as mentioned before, but the pore size distribution shifts to the smaller side. As a result, the strength and the resistance to creep are increased. The increase of creep is limited to a narrow range by compensating above-mentioned factor of increasing the creep for a factor of decreasing it.

The dynamic Young's modulus of cement paste is about half that of aggregate depending upon the type of it and accordingly the substantial increase of the quantity of cement paste in unit volume of concrete lowers the dynamic Young's modulus of concrete.

Conclusion

The hydration reaction, hardened structure and pore structure of concrete prepared by substituting various mineral powders for 230 to 300 kg/m^3 as part of fine aggregate have been studied and the relationships between those items and the physical properties of concrete have been investigated.

(1) The hydration reaction of cement, hydration product and hardened structure of the concrete prepared by substituting the mineral powder for part of fine aggregate are not substantially different from those of concrete prepared by using fly ash cement, blast-furnace slag cement and inert mineral powder-blended cement with high content of

blending component except for the densification of hardened structure by the filling effect of mineral powder itself.

(2) The mineral powder is uniformly distributed over the matrix part in concrete and it fills up the pores, prevents the materials from separating, reduces the size of the hydration reaction products and inhibits the deposition of $Ca(OH)_2$. As a result, the capillary pore as large as 50 nm to 1 μm in diameter are reduced and the formation of the transition zone is inhibited.

(3) In the concrete prepared by substituting slag powder for part of fine aggregate, $Ca(OH)_2$ produced in the hydration of cement is consumed by a reaction with slag to precipitate fine C-S-H from the early age on, which fills up the large-sized capillary pore to form gel pore, thereby densifying the structure of concrete. In the concrete prepared by substituting fly ash for part of fine aggregate, the large-sized capillary pore is mainly filled up with fly ash itself till the age of 28 days in the same way as limestone and silicious stone powders and accordingly the pore size distribution shifts to the smaller side. C-S-H produced in the pozzolanic reaction at the age of 91 days also contributes to densify the structure of concrete by filling up the pore.

(4) The viscosity of fresh concrete is increased by substituting the mineral powder for fine aggregate and the fluidity of it is lowered by it. The quantity of a chemical admixture required for obtaining specified slump is, therefore, increased. The added quantity of it vary according to the kind of mineral powder, and the higher the adsorbed quantity of the chemical admixture, the larger the addition is. For instance, the added quantity of it to the fresh concrete prepared using fly ash was approximately 1.5 times as much as limestone powder.

(5) The strength of concrete prepared by substituting the mineral powder for part of fine aggregate, particularly by substituting slag, is higher than that of concrete without substitution of it. The compressive strength of the concrete prepared by substituting fly ash at the age of 91 days differs by 10.0 MPa from those of concrete prepared by substituting limestone and silicious stone powders. The increase of strength may be mainly caused by the filling up of pores in concrete with the mineral powder, the prevention of the movement of pore solution to the aggregate and of the deposition of large-sized $Ca(OH)_2$ crystal on the surface of aggregate, and the densification of the structure of the concrete in the case prepared by substituting slag and fly ash powders with pozzolanic reactivity by increasing the quantity of C-S-H.

(6) It is considered that the slight increase of the creep of the concrete prepared by substituting fly ash for part of fine aggregate is caused by the offsetting of the increase of practical quantity of cement paste in concrete by the increase of the strength by shifting the pore size distribution of concrete to the smaller side, and that the decrease of the dynamic Young's modulus is caused by the increase of practical quantity of cement paste with the dynamic Young's modulus about half that of the aggregate.

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