Durability and Micro Structure of 200N/mm^2 Grade Ultra-high Strength Fiber Reinforced Concrete

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ABSTRACT
Resulting from investigation about durability of ultra-high strength fiber reinforced concrete of 200N/mm^2 grade (hereinafter UFC is abbreviated) using high strength additives with ettringite generation (hereinafter AFT is abbreviated) system, it became clear that as for diffusion coefficient of chloride ion 1.33×10^{-10}cm^2/sec and gas permeability coefficient 4.5×10^{-20} m^2, the values are small two or more orders of magnitude than its of conventional high strength concrete with water cement ratio 0.30. In addition, durability of freezing-thawing cycles and resistance of alkali-silica reaction are very high. On the other hand, as for the micro structure, the total pore volume is decreased by use of AFT, and pore size distribution is shifted to smaller side and does consolidation. Also, the penetration resistance of chloride ion is found relevance in pore equal to or less than pore diameter of 50-60 angstrom(0.0050-0.0060µm).
Keyword; durability, ultra-high strength, fiber reinforced concrete, micro-structure

1. Introduction
There are lots of papers[1,2] about AFT system as one of high strength concrete technologies. As a result of having examined various durability such as diffusion coefficient of chloride ion, gas permeability coefficient, freezing-thawing cycles, and resistance for alkali-silica reaction of UFC using AFT, it is clearly obvious that UFC has the far superior durability compared with conventional high strength concrete with water cement ratio 0.30.This paper indicates results of various durability tests and inspected a characteristic of pore structure of UFC with AFT system.

In addition, by using specimen in which chloride ion migrated by electrophoresis for 6 months, pore structures of a penetration area of chloride ion were compared with those of a non-penetration one and it clarified relevance about penetration resistance of chloride ion.

This paper indicates results of various durability tests and inspected a characteristic of pore structure of UFC with AFT system.

2. Experiment method
2.1 Materials
As a binder, portland cement and ettringite generating high strength additive (hereinafter AFt system additive is abbreviated), aggregate of

Table 1 Chemical composition of binder (wt%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	Na_2O	K_2O
65.4	8.8	2.7	16.3	4.0	0.35	1.36

crushed sand of non alkali-silica reaction of maximum dimension 2.5mm, polycarbonate high-range water reducing agent, fine steel fiber with tensile strength 2000 N/mm^2 were used. Chemical composition of mixture with portland cement and AFt system additive as a binder is indicated in Table1.

2.2 Durability test methods

Items of various durability tests and a list of testing method are indicated in Table 2 and Table 3.

As a mixing proportion of concrete, binder / sand ratio was 1/0.8, water (including a high-range water reducing agent)/binder ratio (hereinafter W/B is abbreviated) was 0.16, and fine steel fiber was added 1.75vol%. Table flow value (there is no fall in JIS R 5201) of fresh concrete was 250±20mm. Specimens were cured in 20 degrees Celsius for 24 hours after casting and after demolded, the specimens were performed steam curing for highest temperature 85 degrees Celsius for 20 hours.

In addition, specimens in chloride ion migrated by electrophoresis were casted in 0.16, 0.20, 0.30 of W/B. The osmosis depth of penetrating chloride ion was measured by the wide area SEM.

2.3 Measuring method of pore size distribution and hydration system

Investigating the influence that an AFt system additive gave to pore structure of hardened concrete, the specimens which changed W/B with or without the AFt system additive were cast on same mixing proportion(without steel fiber) and curing method of the durability test methods. In addition, highest temperature 85 degrees Celsius for 48hrs and 75 degrees Celsius for 20hrs and 90 degrees Celsius for 48hrs were added to investigate influence of a steam curing condition.

The measurement of pore size distribution was performed by the aid of polosimeter with a mercury penetration, and a test sample was taken out a particle size of 2.5-5.0mm from crushed hardening concrete and was performed by suction drying for 48 hours. Furthermore, powder X-ray diffraction in hydration product, SEM-EPS in crystalline form and structure element were observed in the penetration area and the non-

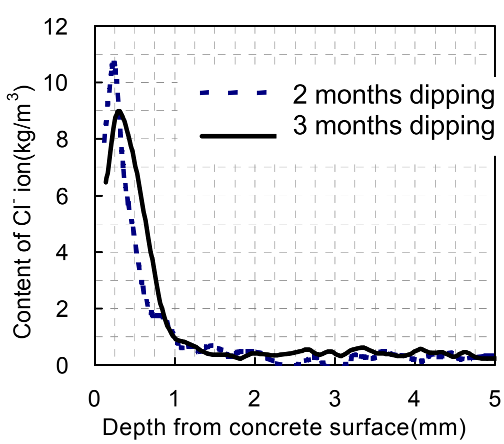

Fig 1 Concentration of Cl^- ion

Table 2 Durability test methods

Item	Method	Specimen dimensions	W/B by weight	Fiber
Penetration resistance of chloride ion	Dipping into 10% NaCl solution	100×100×400mm	0.16	Yes
	Electrophoresis (JSCE-G571-2003)	dia.100×50mm	0.16,0.20, 0.30	No
Air permeability	RILEM TC116-PCD	dia.150×50mm	0.16	Yes
Freezing and thawing durability	JIS A 1148 (A-type method)	100×100×400mm	0.16	Yes
ASR resistance	JIS A 1146 (R_2O=12.8kg/m^3)	100×100×400mm	0.16	Yes

Table 3 Durability test results

Item	A summary of a test result
Penetration resistance of chloride ion	1)Apparent diffusion coefficient of chloride ion; 2 months : 2.38×10^{-10} cm^2/sec 3 months : 1.33×10^{-10} cm^2/sec 2)Penetration depth of electrophoresis (6 months); W/B=0.30(strength is 129.2N/mm^2) : 22mm W/B=0.20(176.1 N/mm^2) : 12mm W/B=0.16(209.7 N/mm^2) : 6mm
Air permeability	Air permeability coefficient : $4.5\times10^{-20}m^2$
Freezing and thawing durability	Relative dynamic modulus of elasticity : 100% Change ratio of weight : 0% (Both after 1000 cycles)
ASR resistance	ASR expansion ratio : 44×10^{-6} (after accelerated curing for 26 weeks)

penetration area which chloride ion infiltrated by electrophoresis.

3. Experiment result and discussion

3.1 Result of durability test

Depth of penetration and concentration distribution of chloride ion by dipping in 10wt% NaCl salt water are shown in Figure1 for Table3 with the

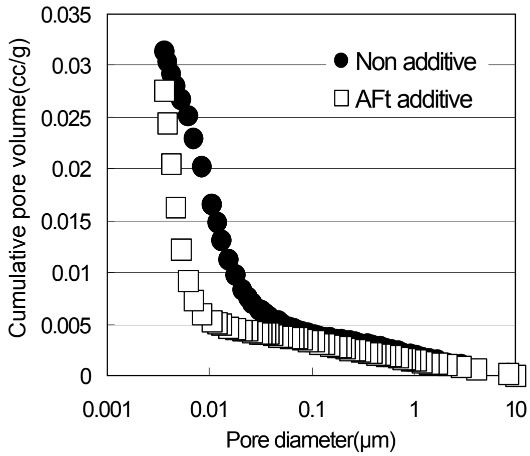

Fig 2 Cumulative pore volume

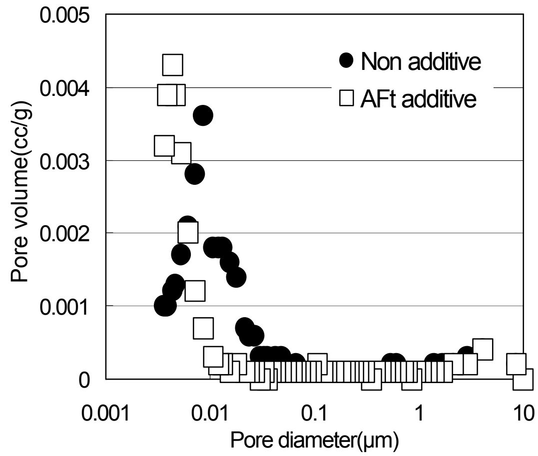

Fig 3 Pore size distribution

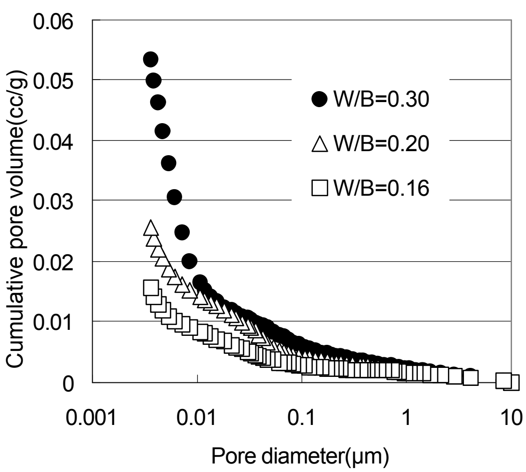

Fig 4 Cumulative pore volume

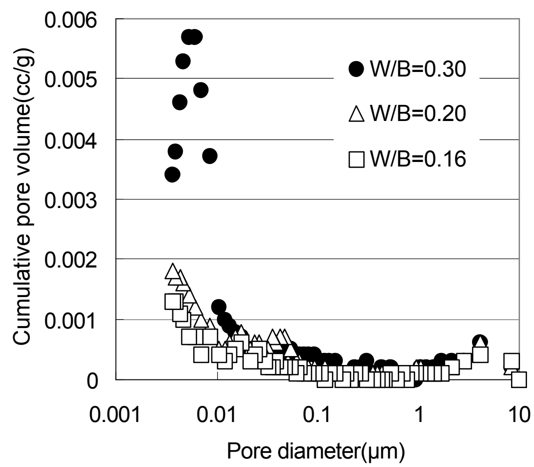

Fig 5 Pore size distribution

durability test result of concrete with 205.4N/mm^2 compressive strength in age 3 days after steam curing.

As for the apparent diffusion coefficient of chloride ion calculated by Fick's second law from depth of penetration by dipping in 10wt% NaCl salt water, its values are 2.38×10^{-10}cm^2/sec in two months dipping and 1.33×10^{-10} cm^2/sec in three months. The diffusion coefficient showed the tendency that became small so that age became long, and the values are small two or more orders of magnitude than apparent diffusion coefficient[4] of conventional high strength concrete with water cement ratio 0.30.

Air permeance coefficient calculated in Darcy's law from a gas transmission test was 4.5×10^{-20}m^2, and its value was small three or more orders of magnitude to be compared with the value[3] 1.0×10 $^{-17}$m^2 of ordinary high strength concrete of W/B=0.30.

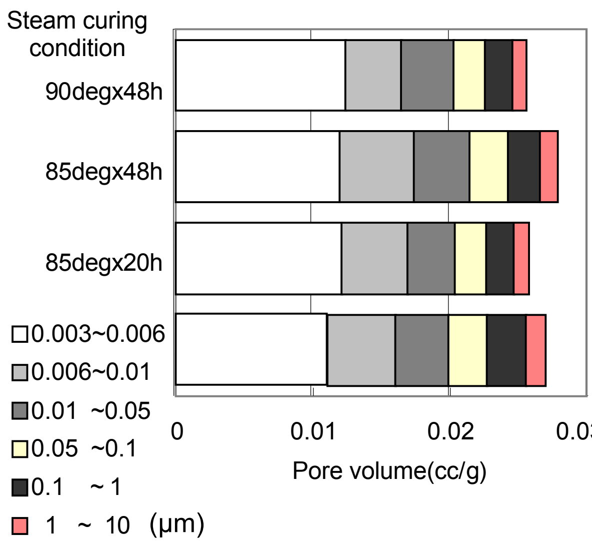

Fig 6 Pore size and steam curing

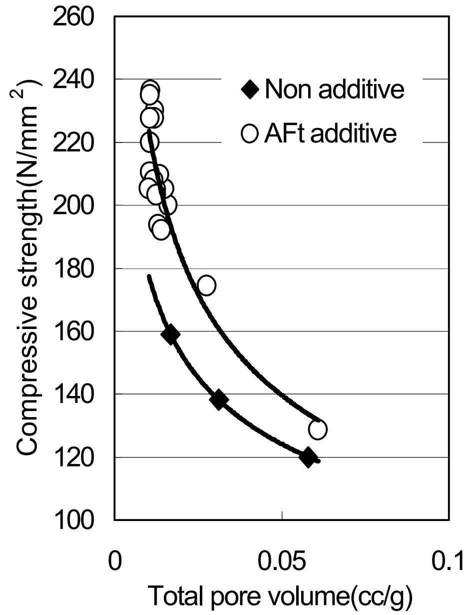

Fig 7 Strength and pore volume

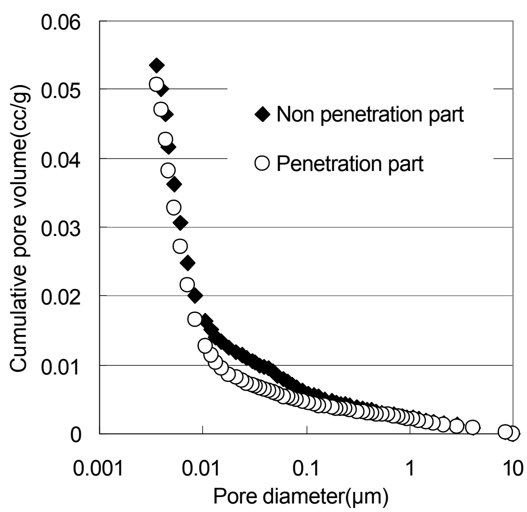

Fig 8 Influence of Cl^- on total pore

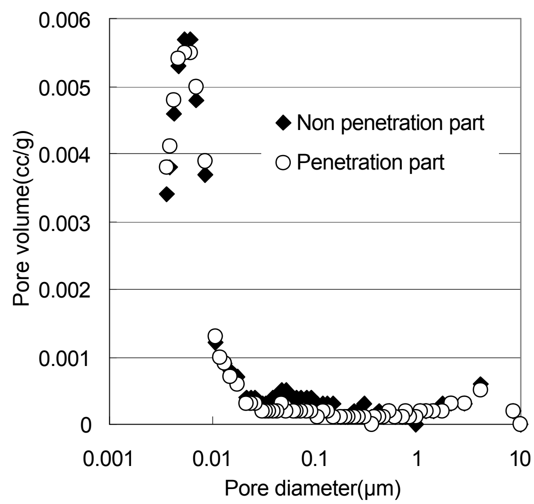

Fig 9 Influence of Cl^- on pore distribution

Even if 1,000 cycles were elapsed as a freezing-thawing test, a dynamic modulus of elasticity and a gravimetric change were very small, and the durability older than 100 years was provided in a judgment of frost damage exposure of "Recommendations for Self Compacting High Strength Concrete Structures(Draft)" of Japan Society of Civil Engineers. There was a little quantity of expansion in age 26 weeks by an ASR accelerated test, and it became clear that there was not danger of alkali-silica reaction in aggregate of division "A".

3.2 Result of pore size distribution and hydration system

(1)Pore structure of concrete with AFT system additive

A cumulative pore volume and pore size distribution by presence of an AFt system additive in case of W/B=0.20 are shown in Figures 2 and 3. In comparison of total pore volume with 0.0313cc/g(compressive strength 138.2N/mm^2) in case of non additive, there is slightly few it with 0.0276cc /g(compressive strength 174.5N/mm^2) in AFt system additive. In addition, a peak of pore size distribution shifts to 0.0043μm(43 angstrom) in AFt system additive smaller than 0.0085μm(85 angstrom) in case of non additive, and concrete in AFT system additive makes more dense micro-structure.

(2)Influence of W/B ratio

A cumulative pore volume and pore size distribution by adding an AFt system additive in case of W/B=0.16, 0.20, 0.30 are shown in Figures 4 and 5. Total pore volume decreases so that W/B ratio lowers due to 0.0610cc/g of W/B=0.30, 0.0276cc/g of W/B=0.20 and 0.0146cc/g of W/B=0.16. Furthermore, whereas there is a peak to 0.0060μm (60 angstrom) in W/B=0.30, there is a peak with smaller size to 0.0043μm (43 angstrom) in W/B=0.20 and to 0.0036μm (36 angstrom) in W/B=0.16. As W/B ratio lowers, pore size distribution shifts to smaller side and concrete makes more dense micro-structure.

(3)Influence of steam curing

In the case of W/B= 0.16 adding AFt system additive, the influence of a steam curing condition upon pore structure was shown in Figure 6. Whereas compressive strength was 209.8N/mm^2 provided in retention time 20hrs at curing temperature 85 degrees Celsius as a basic steam curing condition, it was 210.6N/mm^2 in 85 degrees Celsius for 48hrs, 206.9N/mm^2 in 75 degrees Celsius for 20hrs, 208.7N/mm^2 in 90 degrees Celsius for 48hrs. Those strength differences are small, and a large difference is not recognized in a total pore volume and pore size distribution either. In addition, relations of a total pore volume and compressive strength included the cases that W/B ratio lowers smaller are shown in Figure 7. Two curves different from AFt system additive in non additive are shown in Figure 7, and the compressive strength with AFt system additive is higher than it without additive, even if the total pore volume is same. In addition, whereas strength difference of two curves on 0.06cc/g of total pore volume is only 15N/mm^2, difference on 0.02cc/g is 40N/mm^2 larger. An AFt system additive strengthens hydration structure itself in a high strength region and its structure does densification.

As for reasons, it is thought about 1)enhancement effect by the ettringite which is higher strength than C-S-H gel, 2)effective micro-pore fill being performed by hydration of the later silicate phase after ettringite generates in early period of hydration and fills a comparatively large pore[2], 3)increasing quantity of generation of C-S-H because of reaction with $Ca(OH)_2$ which the active silica in an AFt system additive generates, 4)decrease a $Ca(OH)_2$ crystal of hexagon placoid to be weak points of a hardening concrete.

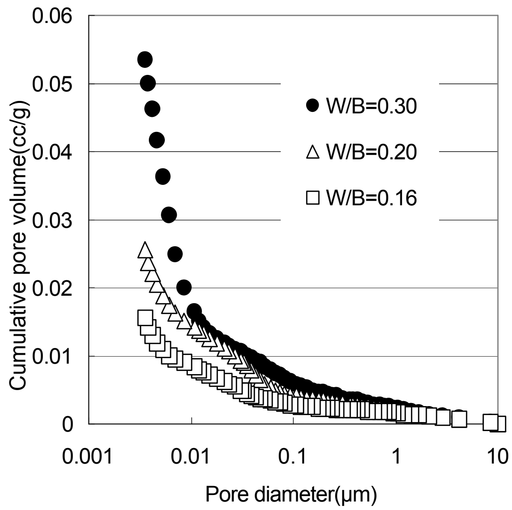

Fig 10 W/B and pore volume

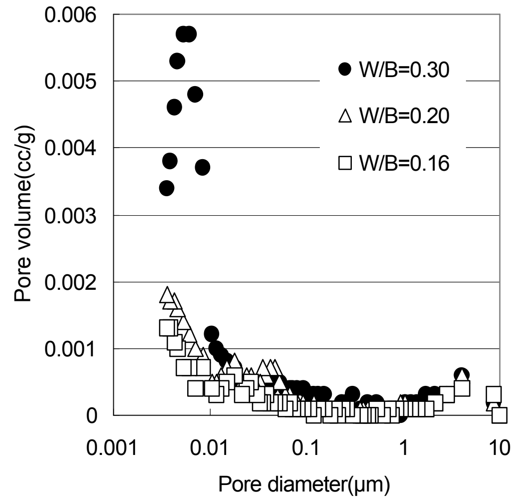

Fig 11 W/B and pore size distribution

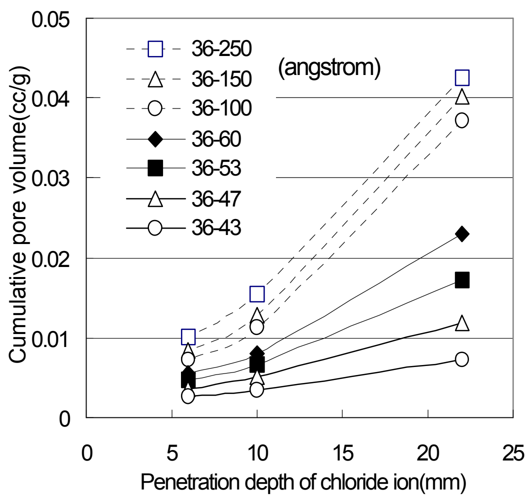

Fig 12 Cl⁻ penetration and pore diameter

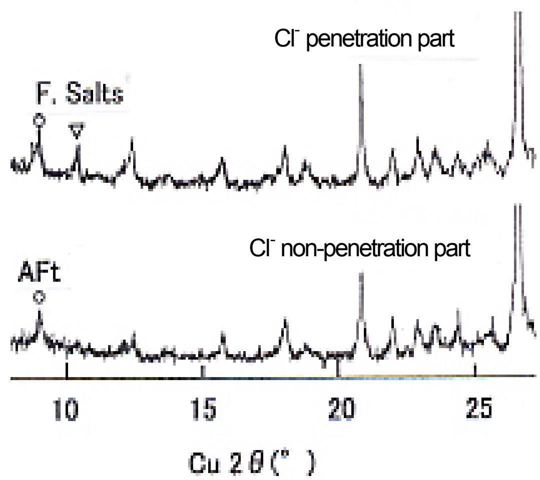

Fig 13 Powder X-ray diffraction

(4)Micro-structure of chloride ion penetration and non-penetration area

A cumulative pore volume and pore size distribution to be compared a non-penetration area with a penetration area of chloride ion of concrete of W/B=0.30 are shown in Figures 8 and 9. Decreasing pore volume, in which size is equal to or less than 0.1μm, by chloride ion penetrating is shown.

Total pore volumes decrease so that W/B ratio lowers same as above-mentioned Figures 6 and 7 by the result that comparison (Figures 10 and 11) made a cumulative pore volume and pore size distribution of a non-penetration area according to every W/B. When 0.054cc/g of W/B=0.30 is assumed 1.00, total pore volumes of W/B=0.20 and 0.16 decrease greatly with 0.48, 0.30 each. In addition, the peak of pore size distribution shifts to 0.0036μm (36 angstrom) in less than 0.20 of W/B ratio whereas there is a peak to 0.0050-0.0060μm (50-60 angstrom) in W/B=0.30, and densification of lower W/B ratio advances more. Furthermore, relationship between total pore volume in a non-penetration area of concrete and apparent diffusion coefficient calculated from depth of penetration of chloride ion is shown in Figure 12.

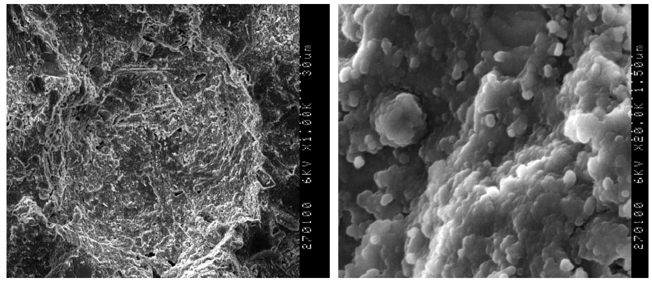

Fig 14 Spherical C-S-H by SEM

The relationship between apparent diffusion coefficient and pore diameter equal to or less than 43 angstrom(0.0043μm) is recognized as a straight line, and this linearity is lost so that a pore diameter is larger than 43 angstrom(0.0043μm).

Prof. Goto found out that there is straight-line relationship in a logarithm of apparent diffusion coefficient of chloride ion and pore volume of less than pore diameter of 40 angstrom(0.0040 μm), strong correlation of pore volume equal to or less than a diameter of 40 angstrom(0.0040 μm) with diffusion coefficient of chloride ion. This experiment was shown to be similar to Prof.Goto's result. In addition, Prof. Goto showed that resistance for diffusion of chloride ion in pore volume equal to or less than a diameter of 40 angstrom(0.0040 μm) is larger than in one over 40 angstrom (0.0040μm). On the other hand, this experiment got a reverse result. This reason is considered to be caused by that there is no continuous large pore which chloride ion detours and diffuses in 200N/mm^2 grade concrete.

Generation of AFt is recognized in both with penetration area and non-penetration area of chloride ion by a powder X-ray diffraction result (Figure 13). In addition, Friedel's salt is generated to penetration area of chloride ion.

From an observation result of the pore inside of 30-50μm with SEM(Figure 14), minute spherical C-S-H(III) is recognized to be generated in chloride ion non-penetration area during steam curing, and smooth surface appearance is observed generally. On the other hand, new hydrate is generated in pore of penetration area of chloride ion, and the crystalline form is diversity such as acerate of around 1.0μm in length, form of petal. This new hydrate is C-S-H and chloride ion is detected on the crystal surface by an elementary analysis result of ESP.

It is considered that generation of new C-S-H and Friedel's salt can make hydration structure to be densification that pore volume equal to or less than 0.1μm of diameter slightly continually lowers by penetration of chloride ion. In addition, because chloride ion is adsorbed on the surface of this C-S-H, penetration of chloride ion makes new hydrate generate , and a pore diameter is diminished. Furthermore, chloride ion itself is adsorbed by physical / chemical, and it is suggested with improve penetration resistance by itself.

4. Summary

1)Chloride ion diffusion coefficient and air permeance of the 200N/mm^2 grade ultra high strength fiber reinforced concrete by use of AFt system additive show a value of small two or more orders of magnitude than high strength concrete of W/B=0.30, and the durability in freezing-thawing resistance and ASR resistance is recognized to be very high.

2)An AFt system additive can promote densification of hydration structure due to decrease a total pore volume and shift the distribution of pore diameter to the parvus side.

3)Correlation of pore equal to or less than 43 angstrom(0.0043μm) with penetration resistance of chloride ion are shown and the resistance grows bigger as pore volume of lower than 43 angstrom(0.0043μm) is less.

4)By penetration of chloride ion, new C-S-H and Friedel's salt generate it all over the pore, and pore diameter is made small.

5)Chloride ion itself is adsorbed by physical / chemical and penetration resistance is improved by itself.

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