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EXPERIMENTAL STUDIES ON BASIC PROPERTIES OF CONCRETE USING TiO₂ AS ADMIXTURE

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ABSTRACT

As buildings need to have not only high design but also durability, it's necessary to think about multifunction materials. In this study, for the purpose of clarifying the basic properties of mortar and concrete using titanium oxide (TiO₂) as an admixture, the authors have carried out experiments on the fresh and hardened properties focusing on the W/C and TiO₂ ratios. The results suggest that workability properties could be satisfied and higher strength achieved by substituting optimum levels of TiO₂. In addition, when examining brightness retention it was found that mortar containing 15% TiO₂ had the best resistance to brightness degradation and self-cleaning performance with TiO₂ as a photocatalyst. As a result, using proper TiO₂ as an admixture in mortar or concrete can be useful for giving additional performance such as brightness retention and self-cleaning effects on the surface, as well as strength development and crack control of the specimen itself.

Keywords: Titanium oxide powder, Admixture, White Portland cement, Photocatalyst.

1. INTRODUCTION

Concrete, steel and wood are principal materials in the construction field and have three important properties: safety, workability and durability. These days, however, buildings need not only these three properties but also additional (+α) performance such as beautiful appearance, saving energy in order to increase working efficiency, recycling in order to use resources repeatedly without waste and with low cost, and so on. Furthermore, judging from the fact that buildings in cities have been rebuilt one after another and are becoming more complicated in design and shape, increased multifunction and high performance of building materials is growing in importance. When we want concrete to have these properties, we usually use admixtures such as blast furnace slag, silica fume, fly ash and titanium oxide (TiO₂). TiO₂ is well known for its pigment, the whiteness of which is incomparable with other materials. However it has also attracted a great deal of attention as a “photocatalyst” with various positive effects, such as water purification, gas decomposition,

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brightness retention and self-cleaning. Thus, it is used in a variety of fields and the global scale of the photocatalyst market is expected to expand. In the construction field, we use it in paint or coating materials. However, it cannot be used more than approximately 10 years because the paint is easily worn down and there are many problems related to its use, since the painted base materials are not limited only to organic substance.

Here, the authors propose inorganic concrete using TiO_2 as an admixture because we believe the concrete has good whiteness and photocatalytic effects such as brightness retention and self-cleaning, which can keep the building's appearance clean without any maintenance. Furthermore, we expect that durability and safety will improve with TiO_2 included in the concrete. Nevertheless, there have not been many studies on TiO_2 concrete and the data is limited.

In this study, in order to clarify the basic properties of mortar and concrete using TiO_2 as an admixture, we have carried out experiments on the fresh properties, strength properties, drying shrinkage, carbonation depth and brightness retention.

2. EXPERIMENTAL

For the investigations on workability, safety, durability and brightness retention, we carried out two sets of experiments Step 1: Characteristics of TiO_2 mortar and Step 2: Basic properties of TiO_2 concrete.

2.1. Materials

The materials used in Step 1 and Step 2 are given in Table 1, Figure 1 and Picture 1. Fine aggregate A is used only in experiments on brightness retention in Step 1, and fine aggregate B is used for the other experiments. Coarse aggregates and chemical admixtures are only used for the experiments in Step 2.

2.2. Experimental process and test pieces

Experimental items and the size of test pieces are given in Table 2 and Figure 2. Additionally, the experimental process for measuring neutralization depth is shown in Figure 3.

Table 1: Experimental materials

Cement	White Portland Cement (C) Density: 3.05g/cm ³ , Surface Area: 3350cm ² /g
Fine aggregate A	Silica sand in Tochigi, Japan (S) Density: 2.63g/cm ³ , Water adsorption rate: 0.27%
Fine aggregate B	River sand in Kinugawa, Japan (S) Density: 2.58g/cm ³ , Water adsorption rate: 2.25%, FM: 2.28
Coarse aggregate	Crushed Limestone in Shuho, Japan (G) Density: 2.68g/cm ³ , Water adsorption rate: 0.94%, Maximum size: 20mm
Admixture	Titanium Oxide (type of Anatase) Density: 3.9g/cm ³ , BET surface area: 72,533cm ² /g, Particle size: 0.509μm
Chemical admixture	High Range AE Water Reducing Agent (SP)
	Polycarboxylic acids-based compound and Glycol ether derivative
	Air Entraining Agent (AE) Alkyl ether system anion surfactant

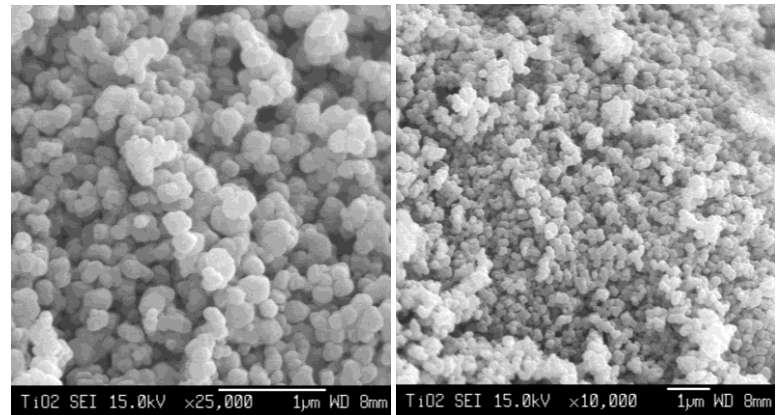
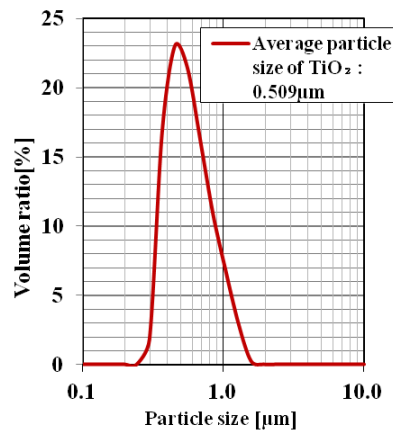


Figure 1: Particle size distribution of TiO_2

Picture 1: SEM photomicrographs of TiO_2 (Left and right magnifications are 25,000 and 10,000)

Table 2: Experimental items and the size of specimens

Step	Experiment	JIS ^{※1}	Testing age	Size of specimens	Form removal	Curing method
1	Mortar-flow	R 5201	-	-	-	-
	Compressive and flexural strength	R 5201	7.28.56.91 day	4×4×16 cm	1 day	under 20°C water
	Carbonation depth	A 1153	(Accelerated) 4.6.8.13 week	4×4×16 cm 10×10×40 cm		(refer to Fig.3)
	Brightness retention	Z 2381	2.6.9.12.15 month	10×15×1 cm		Atmospheric exposure ^{※2}
2	Slump	A 1101	-	-	-	-
	Bleeding	A 1123	-	-	-	-
	Setting time of concrete	R 5201	-	-	-	-
	Compressive strength	A 1108	3.7.28.91 day	φ10×20 cm	1 day	under 20°C water
	Static modulus of elasticity	A 1149				
	Drying shrinkage	A 1129-3	7.28.56.91.182 day	10×10×40 cm		under 20°C water

※1) Testing method according to JIS, it shows standard number of JIS.

※2) The specimens was exposed on the campus of Shibaura Institute of Technology.

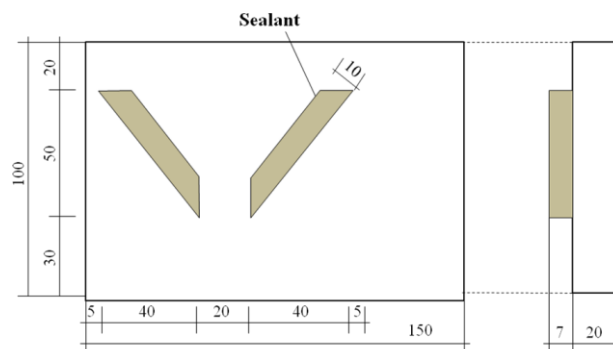


Figure 2: Test piece for brightness retention experiment

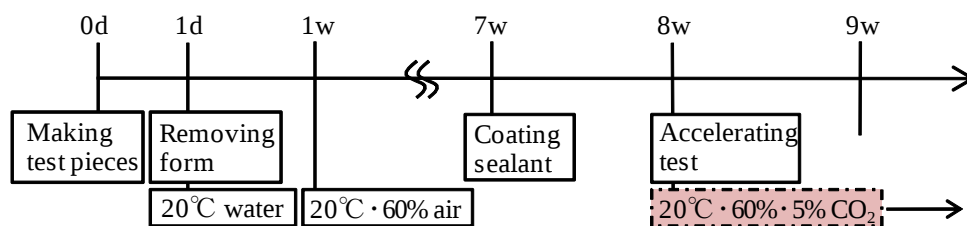


Figure 3: Experimental process for measuring carbonation depth

2.3. Mixture proportion

2.3.1. Step 1: Characteristics of TiO₂ mortar

The mixture proportions for Step 1 are shown in Table 3. For the experiment on brightness retention, W/C (W/B) was set at 50% and TiO₂ partially replaced the fine aggregates at 5%, 10%, 15% and 20% by weight of fine aggregate A. On the other hand, for W/C (W/B) of 50% and 70%, the amount of TiO₂ in mortar partially was replaced cement and fine aggregate at 10% and 20% by weight of cement and fine aggregate B for the other experiments.

2.3.2. Step 2: Basic properties of TiO₂ concrete

The mixture proportions for Step 2 are shown in Table 3. The amount of TiO₂ in concrete was 10% and 20% by weight of fine aggregate B and W/C (W/B) was set to 30%, 40% and 50%.

Table 3: Mixture proportions

	Name	W/C [%]	Replaced by TiO ₂ [%]		Unit weight [kg/m ³]					SP [C×%]	
					W	C	TiO ₂	S	G		
Step 1	M50	50	0		284	568	0	1250			
	M50-5a		Fine aggregate	5			28	1222			
	M50-10a			10			57	1193			
	M50-15a			15			85	1165			
	M50-20a			20			114	1136			
	M50-10b		Cement	10		511	57	1250			
	M50-20b			20		454	114				
	M70	70	0		305	435	0	1305			
	M70-10a		Fine aggregate	10			44	1261			
	M70-20a			20			87	1218			
	M70-10b		Cement	10		391	44	1305			
	M70-20b			20		348	87				
	Step 2	C30 ^{※3}	30	0		160	534	0	601	1034	1.25
		C30-10a		Fine aggregate	10			53	565		
C30-20a		20			107			531			
C30-10b		Cement		10	481		53	604	1043		
C30-20b				20	428		107	609	1048		
C40 ^{※3}		40	0		174	435	0	635	1051	0.6	
C40-10a			Fine aggregate	10			44	606			
C40-20a				20			87	578			
C40-10b			Cement	10		392	44	637			1056
C40-20b				20		348	87	642			1059
C50 ^{※3}		50	0		167	334	0	738	1051	0.6	
C50-10a			Fine aggregate	10			33	717			
C50-20a				20			67	694			
C50-10b			Cement	10		301	33	740			1059
C50-20b				20		267	67	743			1059

※3) Target slump and air for C30, C40 and C50 are 18.0±1.5cm and 4.5±1.0%.

3. RESULTS AND DISCUSSION

3.1. Step 1: Characteristics of TiO₂ mortar

3.1.1. Mortar flow

The mortar flow values when using different TiO₂ contents became smaller as the proportion of TiO₂ replacing the fine aggregate B increased, with a decline of 4~18% at the same W/C (W/B). It is considered that the decline was caused by the large difference in surface area which led to a disparity in water absorption between cement and TiO₂. In general, materials with a larger surface area have high absorbency and thus the mortar flow decreases when there is not enough liquid water in the mortar.

3.1.2. Compressive and flexural strength

The effect of TiO₂ replacement rate on the compressive and flexural strength of mortar is shown in Figure 4. As the aggregate replacement amount of TiO₂ increases, the compressive and flexural strength also increased. Considering the TiO₂ particle size, TiO₂ possibly entered into capillary voids and filled the mortar. Declines in strength for “10b” and “20b” are conjectured to be caused by the decreasing cement content which leads to the mortar hardening.

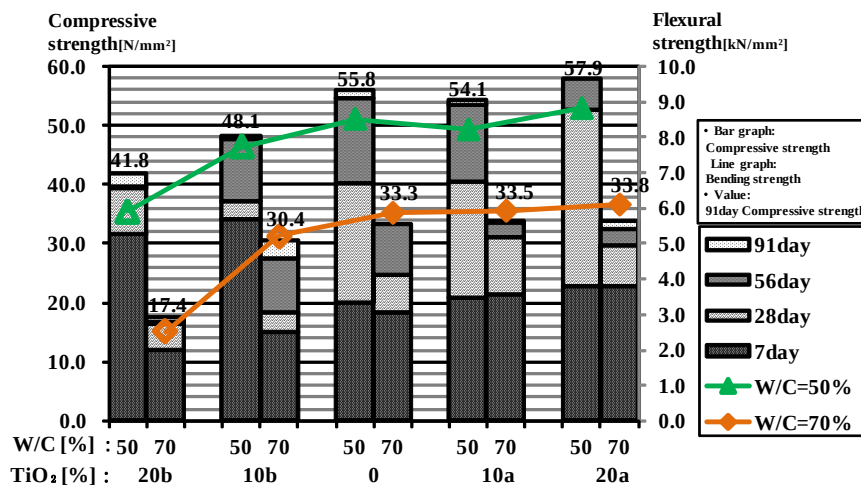


Figure 4: Compressive and flexural strength of mortar

3.1.3. Carbonation depth

According to Figure 5 and Picture 2, which were taken after 13 weeks of accelerated age, the carbonation depth was 6.6 ± 1.5 mm for W/C(W/B)=50% and 12.9 ± 2.4 mm for W/C(W/B)=70%. Therefore, there was not such a large difference in carbonation depth caused by TiO₂ except in the case of “20b.” In the case of “20b,” W/C(W/B)=50% and 70% showed 12.0 mm and 21.1 mm of carbonation depth, respectively. This may be due to the reduction in a unit cement and alkaline ingredient as a result of replacing cement with TiO₂.

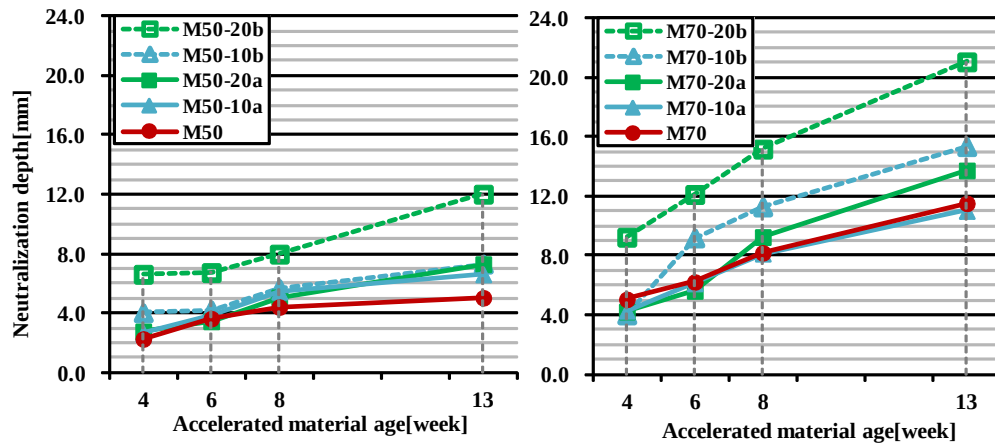
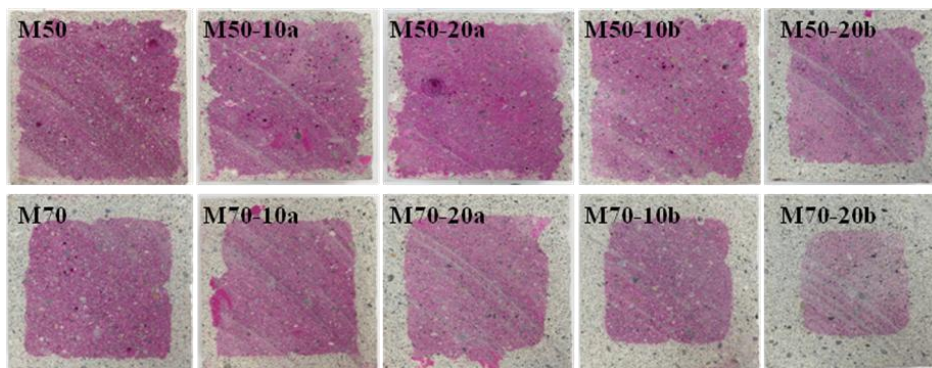


Figure 5: Carbonation depth



Picture 2: Cross-sectional result of carbonation depth of mortar (accelerated age of 13 weeks)

3.1.4. Brightness retention

Figure 6 shows the brightness retention by different TiO_2 aggregate replacement rate. Mortar containing 15% of TiO_2 has the greatest resistance to brightness degradation, and a comparison of test specimens facing south or north shows that the former has better brightness retention.

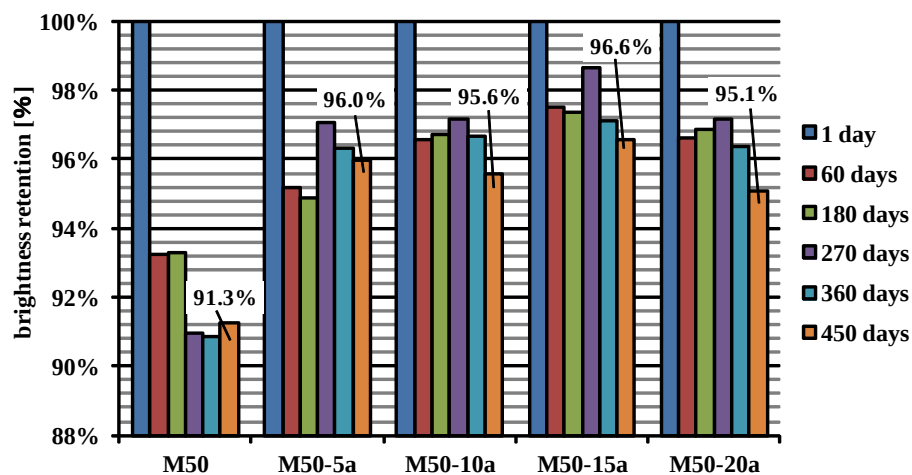


Figure 6: Brightness retention

3.2. Step2: Basic properties of TiO₂ concrete

3.2.1. Slump, bleeding and setting time of concrete

The decrease in rate of bleeding compared with non-TiO₂ concrete is 66~92%, and thus there are two possibilities for how TiO₂ behavior affects the inside of concrete. One possibility is that TiO₂ has the ability to physically retain water; whereas the other possibility is that TiO₂ makes concrete very compact chemically or physically because of its fineness. When examining the setting time of fresh concrete with different TiO₂ at the same W/C (W/B), it was found that the starting and finishing time of setting became 16~21 and 33~41 minutes faster than non-TiO₂ concrete. These results indicate that TiO₂ obstructs hydration reaction of cement due to some unclarified mechanism. Moreover, the concrete slumps were almost the same when using a small amount of SP, so it can be said that the TiO₂ ratios have little influence on workability.

3.2.2. Compressive strength and static modulus of elasticity

When replacing fine aggregate with TiO₂, an increase in compressive strength and static modulus of elasticity from ages 3 to 91 days could be seen, as shown in Figure 7. The reason for the increase in hardness is considered to be the same as in the case of mortar.

3.2.3. Drying shrinkage

As shown in Figure 8, the drying shrinkages of all test specimens at 182 days were under 8×10^{-4} , the standard design level written in JASS 5. Furthermore, the drying shrinkages of “C30-10a” and “C30-20b” were almost the same as the case of noTiO₂ at all. It will be necessary to further investigate the influence of TiO₂ for better understanding the effect on crack reduction in the future.

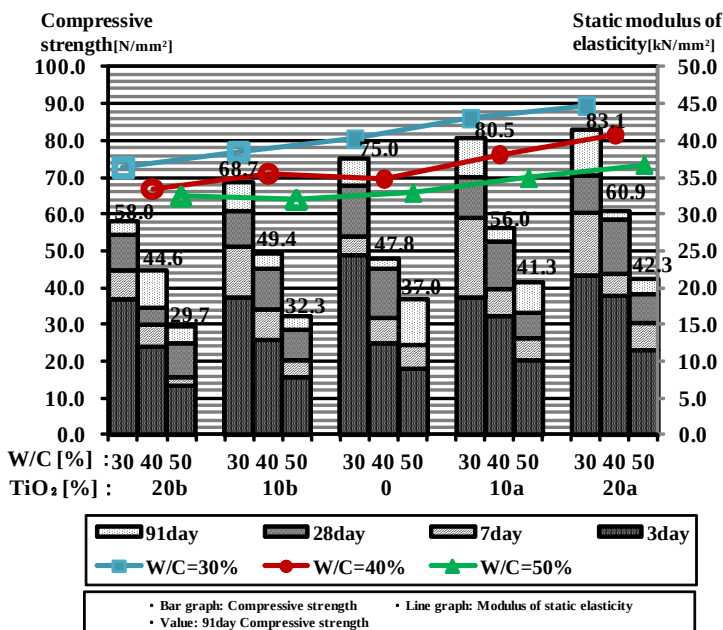


Figure 7: Compressive strength and static modulus of elasticity

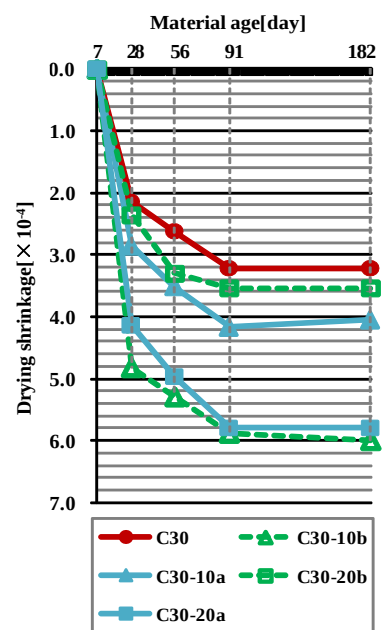


Figure 8: Drying shrinkage of concrete

4. CONCLUSION

In this paper, the following results were found:

(1) With regards to fresh properties,

- ✓ When using TiO_2 mortar-flow for the same W/C (W/B) was 4~18% smaller than for the non- TiO_2 of mortar.
- ✓ The slump could be adjusted easily by using SP regardless of the TiO_2 ratios.
- ✓ The bleeding was 66~92% smaller than non- TiO_2 concrete.
- ✓ The setting time became faster than non- TiO_2 concrete.

(2) With regards to the hardened surface properties,

- ✓ The brightness retention became higher and TiO_2 mortar with 15% replacement of aggregates showed the best resistance to brightness degradation.

(3) With regards to the hardened inner properties,

- ✓ In concrete with replacement of fine aggregate, the compressive strength was 7~27% greater and the static modulus of elasticity was 6~17% greater than for the non- TiO_2 at a material age of 91 days. The increase appeared to be greater for lower W/C (W/B) ratios.
- ✓ The substitution method, ratio, fineness and other factor will need to be investigated to better understand the effect of TiO_2 on drying shrinkage.
- ✓ Mortar with less than 10% TiO_2 had almost the same carbonation depth as non- TiO_2 despite a decrease in unit cement content.

5. ACKNOWLEDGMENTS

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