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?????□????? ? 29 ? 2013 ? 12 ?? Effects of Seawater Mixing and Curing on Strength and Carbonation of Fly Ash Concrete Adiwijaya*, Daisuke Yamamoto**, Amry Dasar*, Hidenori Hamada**, Yasutaka Sagawa**
*Graduate School of Engineering, Kyushu University, Fukuoka, Japan, 819-0395 **Department of Civil and Structural Engineering, Kyushu University, Fukuoka, Japan, 819-0395 In this study, effects of seawater mixing and seawater curing on compressive strength, porosity, and carbonation depth of concrete with 20% fly ash replacement were investigated. Concrete cylinder specimens with water-binder ratio of 0.5

were prepared using natural seawater or tap water as mixing water. At 24 hours after casting, specimen was demolded and followed by different curing conditions, such as tap water curing, seawater curing and air curing in 20 ° C, RH 60% controlled room for 28 days. Result shows that compressive strength of concrete mixed with seawater at 28 days was improved compared with tap water mixed concrete for each curing condition and no significant difference in compressive strength of concrete is observed for tap water curing and seawater curing.

In addition, a good correlation between compressive strength and carbonation coefficient in seawater mixed and tap water mixed concrete was also obtained. 1 . Introduction Seawater contains about 35,000 ppm dissolved salt and total salinity is 3.5%, of which 78% is sodium chloride1),2). It is well known that the presence of chloride ions increases the risk of corrosion of steel bar in concrete. Therefore, it is recommended that seawater should not be used as mixing water for reinforced concrete2),3).

However, in case of unavoidable circumstances, seawater may be used as mixing water for not only for plain

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concrete but also reinforced concrete^{4,5}). The investigation of concrete mixed with seawater or salts water on compressive strength has been reported by several studies. The result of studies may not be agreed whether seawater increases or decreases the strength of concrete. Some studies revealed that the compressive strength of concrete at 28 days increases with seawater or salt water^{6,7}).

On the other hand, it is stated that seawater decreases the 28 days strength of concrete³). Meanwhile, the other researcher reported that the compressive strength of concrete is not affected by type of mixing water^{8,9}). It is obvious that the investigation on compressive strength of seawater mixed concrete is still contradictory among researchers. One of major factors leading to structures □ deterioration is carbonation¹⁰).

Carbonation is the reaction between the hydration products (portlandite and calcium silicate hydrates) dissolved in the pore water and carbon dioxide in the air ¹¹). The result of carbonation may lead to initiation of corrosion because steel surface is not passivated anymore owing to a drop in pH of concrete¹²). The carbonation rate of concrete depends notably on the relative humidity, the concentration of CO₂, the penetration pressure, and the temperature of the environment where concrete is placed^{13,15}). Several investigations on carbonation of fly ash concrete have been done by previous researchers^{14,15,16,17,18}).

However, the discussion on carbonation of seawater-mixed concrete with or without fly ash is not explored. In this study, compressive strength, carbonation, and porosity of seawater and tap water mixed of fly ash concrete under curing in seawater, tap water, and air in 20 °C, RH 60% were measured. This paper also deals with the relation of carbonation, porosity, and compressive strength. 2 . Experimental Program 2.1 Materials Two types of binder were used in this study; Ordinary Portland Cement (OPC) and Fly Ash (FA).

Ordinary Portland Cement and Fly Ash meet the requirements of JIS R 5210 and JIS A 6201, respectively. Chemical compositions of cement and fly ash are depicted in Table 1, whereas the physical properties of concrete materials such as binder, aggregates, and natural seawater are presented in Table 2. 2.2 Mix proportion Four series of concrete mixtures with water-binder ratio of 0.5 using tap water or natural seawater as mixing water were prepared by three curing conditions such as tap water curing, seawater curing, and air curing in 20 °C, RH 60%. Table 3 describes the series of concrete mixture that used in this study.

Mix proportion of concrete specimen was designed according to Japan Society of Civil Engineers Standard⁴). The result of mix proportion was pointed out in Table 4. Table 1 Chemical composition of cement and fly ash Constituents OPC Fly Ash MgO, % 1.31 - SiO₂, % - 60.6 SO₃, % 2.14 - Loss of Ignition, % 1.97 2.4 Total Alkali, % 0.43 - Chloride, % 0.016 - Table 2 Physical properties of materials Material Description Cement (OPC) Density : 3.16

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g/cm³, Specific Surface Area = 3330 cm²/g Fly Ash (Type II) Density : 2.26 g/cm³, Specific Surface Area = 3970 cm²/g Aggregates Sand ; Sea sand Density (SSD) : 2.56 g/cm³ FM = 2.69 , Water Absorption : 1.61% Gravel ; Crushed stone Density (SSD) : 2.84 g/cm³, MSA : 20 mm FM : 6.68 , Water Absorption = 0.71% Seawater Density : 1.022 g/cm³ , Cl⁻ : 18715 mg/ltr , pH : 7.707 2.3 Testing methods 2.3.1

Compressive strength and elastic modulus tests At 24 hours after casting, concrete cylinder specimens of 100 mm in diameter and 200 mm in height were demolded, then cured by tap water, by seawater, or by air curing in the 20 °C, R.H. 60% controlled room. After 28 days curing, compressive strength and elastic modulus tests of specimens were conducted in accordance with JIS A 1108 and JIS A 1149, respectively. The average compressive strength and elastic modulus of three specimens were determined for each concrete mixture in three curing conditions. 2.3.2

Porosity tests The total pore volume and pore size distribution of concrete specimen were tested by Mercury Intrusion Porosimetry (MIP). After curing for 28 days, concrete cylinder specimens were cut into 5mm-thick slice samples. Subsequently, the fragments were immersed in acetone for 15 minutes to stop further hydration of cement, and then dried in the vacuum desiccator for 2 days. In the MIP test, complete drying of the samples was required to obtain results without error¹⁶). In this study, the maximum applied pressure of MIP test was 33,000 psi (227MPa), and the surface tension and contact angle of mercury was 485 dynes/cm and 130o, respectively.

Both surface tension and contact angle were used in the Washburn equation to convert applied pressure to pore diameter. The pore width corresponding to the highest rate of mercury intrusion pchge ressuio thotho re width¹⁹). After achieving this highest rate of intrusion, mercury has been shown to penetrate the interior of the specimen. Table 3 Specimen series of concrete mixture Mixture Fly Ash (%) Mixing water Curing conditions TW SW AC TW-OPC - TW done done done TW - 20FA 20 TW done done done SW - OPC - SW done done done SW - 20FA 20 SW done done done Notation: TW and SW are tap water, seawater, respectively. AC is air curing in 20 °C, RH 60%.

Done means the experiment was conducted. Table 4 Mix proportion of concrete mixed (kg/m³) Materials TW-OPC TW-20FA SW-OPC SW-20FA W/B, % 50 50 50 50 s/a, % 45 45 45 45 Tap water 160 160 - - Seawater - 165 165 Cement 320 256 330 264 Fly Ash - 64 - 66 Sand 805 795 802 791 Gravel 1087 1074 1083 1068 AE + WR 1.00 1.00 1.03 1.03 Slump, mm 80 95 80 100 Air Cont., % 6.2 5.8 6.0 3.8 Temp., °C 16 17 18 20 2.3.3 Accelerated carbonation tests Accelerated carbonation test was carried out according to JIS A1153.

The concrete prism specimens of 10 x 10 x 40 cm in size were cured in the 20 °C, 60% R.H., controlled room

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for 28 days. After that, the two longitudinal and transversal sides of prism specimens were coated by epoxy resin then the specimens were dried for 24 hours before carbonated in the accelerated chamber at 20 °C and 60% R.H. with 5% CO₂ concentrations. After a certain exposure period for 1, 4, and 8 weeks, the specimens were split and fresh broken surfaces were cleaned from dust and loose particles.

The carbonation depths were determined by spraying a 1% solution of phenolphthalein in ethanol solution onto the concrete surface. In the noncarbonated region, the color of the solution changes into purple-red when pH value is above 9 (11, 16, 18), whereas in the carbonated portion with pH less than 9, the solution remained colorless. The distance between the color change boundary and the concrete surface was measured as the carbonation depth. Twenty readings were recorded from the two side faces of a specimen at 10 mm intervals.

The average of these readings from two specimens was taken to represent the carbonation depth. 3. Result and Discussion 3.1 Compressive strength and elastic modulus Results of 28 days compressive strength testing of concrete specimens are shown in Fig.1. It was observed that 28 days compressive strength of seawater-mixed concrete (OPC) in tap water and seawater curing increases 1.2 times than tap water mixing. Moreover, the strength enhancement ratio of seawater-mixed to tap water-mixed is achieved more than 1.3 for air curing in 20 °C, RH 60%.

These results are corresponding with previous some studies that seawater or salt water increased the compressive strength of concrete (6, 7). This finding suggests that the presence of chloride in seawater assist to accelerate the hydration process of portland cement into concrete thus lead to a more rapid development of strength as it also revealed by several researchers (2, 20). Similarly, seawater-mixed fly ash concrete in seawater and air curing also enhances the compressive strength.

However, the strength enhancement of fly ash mixed concrete with seawater is smaller than seawater-mixed concrete (OPC). This indicates that chemical reaction process of pozzolans such as fly ash in cement paste is generally slower than ordinary portland cement. Further, the compressive strength at 28 days of concrete specimens for all mixture in tap water and seawater curing is nearly similar except the tap water mix fly ash concrete.

This expresses that compressive strength of concrete mixed with tap water and seawater is not affected by type of curing water such as tap water or seawater as also reported by previous investigation (8). In addition, a good performance is obtained on seawater-mixed concrete, which has no significant difference in compressive strength for water and air curing in 20 °C, R.H. 60%.

This exhibits that 28 days compressive strength of seawater-mixed concrete (OPC) is not affected by curing

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types, whether it is cured in water or cured in air in 20 ° C, R.H. 60%. This phenomenon is expected to be due to chemical reaction of ordinary portland cement (OPC) is rapid and the effect of seawater to accelerate the hydration process of cement. Meanwhile, the compressive strength of seawater-mixed fly ash concrete in water curing and air curing in 20 ° C, R.H.

60% is different because the chemical reaction of fly ash is slow. Fig.1 Compressive strength of concrete specimens at 28 days Fig.2 shows results of relationship between compressive strength and elastic modulus at 28 days. Generally, elastic modulus of seawater mixed concrete and fly ash concrete cured in water is slightly larger compared with the tap water mixed. However, seawater mixed concrete cured in air significantly rises 1.14 times than tap water mixed concrete.

This suggests that the effect of seawater mixing on elastic modulus is same as the effect on compressive strength. This can be explained by relation between compressive strength and elastic modulus, that is, higher compressive strength is, higher elastic modulus is. In general, a good linear correlation between compressive strength and elastic modulus is acquired, which is indicated by Japan Society of Civil Engineers⁴). Fig.2 Compressive strength vs. elastic modulus 3.2

Porosity The total volume of pores and pore size distributions obtained by Mercury Intrusion Porosity tests of concrete specimen at 28 days are depicted in Fig.3 and Fig.4. It is shown that seawater mixed with OPC reduces pore volume of concrete compared with tap water mixed. The diminished porosity occurred for all type of curing, in which the reduced porosity for seawater curing or air curing is greater than tap water curing. Similarly, the porosity of fly ash concrete with seawater decreases compared with fly ash concrete mixed with tap water.

This expresses that total pore volume of concrete at 28 days is possibly affected by accelerating the hydration of cement. Fig.3 Porosity of concrete at 28-days Furthermore, it is also found that pore distribution of tap water and seawater mixed concrete with or without fly ash in tap water and seawater curing is not significantly different. This indicates that total pore volume of concrete (OPC) and fly ash concrete is not influenced by curing water. In addition, the maximum porosity of concrete specimen is achieved by specimens cured in air.

This finding is to be logical as hydration of cement paste in air curing is not perfectly hydrated. The relationship between compressive strength and porosity is shown in Fig. 5. Compressive strength increases, then the porosity decreases. In addition, a good correlation is acquired in which R² values are more than 0.90. This suggests that the compressive strength of seawater mixed and tap water mixed concrete with or without fly ash in water curing are influenced by porosity.

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This is also described in previous studies that strength and elasticity of concrete were affected by the total pore volume or porosity²¹). 3.3 Results of Accelerated Carbonation 3.3.1 The depth of Carbonation Fig.6 shows the carbonation development against exposure period in weeks for all concrete mixtures. It was observed that carbonation depth at 4 weeks (28 days) of concrete mixed with seawater is lower than tap water mixed concrete with 75% and 26% reduction for seawater mixed concrete and fly ash concrete, respectively.

This indicates that seawater mixing significantly decreased the depth of carbonation of concrete with or without fly ash. This is expected due to significant enhancement of compressive strength, which is appropriate with previous investigation observed by some researchers that the depth of carbonation decreased significantly with increasing strength of concrete^{16,22}). a) Tap water curing b) Seawater curing c) Air curing in 20 °C, RH 60% Fig.4 Pore size distributions of concrete specimens The effect of fly ash on carbonation depth of concrete with tap water and seawater mixing is also observed, in which the depth of carbonation of fly ash concrete increases up to 9% and 33% for tap water and seawater mixed, respectively compared with normal concrete with OPC.

This explains that replacement of fly ash increases the rate of carbonation of concrete mixed with seawater and tap water, which is clearly agreed with the trend observed by various researchers^{14,16,17,18}). Fig.5 Compressive strength vs. porosity A good relationship between depth of carbonation and exposure duration for all concrete mixture is obtained in which the R² values are more than 0.92. This suggests that the depth of carbonation of seawater mixed and tap water mixed concrete with and without fly ash is linear to the square root of exposure duration in the accelerated carbonation test, and it is not affected by mix proportion of concrete. This result is also revealed by previous researchers¹⁴). Fig.6

Carbonation progress of concrete specimens Fig.6 Carbonation progress of concrete specimens 3.3.2 Relationship between strength-carbonation-porosity As previously described, a linear relation between depths of carbonation and the square root of exposure time is obtained. Thus, the carbonation depth of concrete may be estimated by regression equations using empirical relationship, as follows: $X = C \sqrt{t}$ (1) Where X = carbonation depth of concrete (mm); C = carbonation coefficient (mm/√weeks); and t = exposure period of accelerated carbonation (weeks). From eq.(1) carbonation coefficient at 28 days may be determined, which had been used by many researchers^{14,16,18}). Fig.7

shows the relation between compressive strength and carbonation coefficient of concrete specimens at 28 days. It shows the correlation coefficient is 0.99. This indicates that the compressive strength at 28 days may be used as indicator to evaluate or to predict carbonation coefficient of seawater mixed and tap water mixed concrete with or without fly ash. This finding is also proposed by the others researcher^{14,15,16}). Fig.7 Compressive strength vs. carbonation coefficient Fig.8 Porosity vs.

carbonation coefficient Furthermore, a good correlation between porosity and carbonation coefficient is also obtained in Fig.8. Both relation \square carbonation coefficient - compressive strength \square and \square carbonation coefficients - porosity \square show that the carbonation coefficients decrease with increasing of compressive strength or decreasing of porosity. It is clear that compressive strength and carbonation coefficient of seawater mixed and tap water mixed concrete with or without fly ash may be controlled by the porosity. 4 . Conclusions Based on results of investigation, the following conclusions can be drawn: 1.

Seawater mixing improved 28 days compressive strength of concrete (OPC) and fly ash concrete compared with tap water mixing in tap water curing, seawater curing, and air curing. 2. There is no significant difference in 28 days \square compressive strength between with and without fly ash for seawater and tap water curing. Moreover, compressive strength of seawater mixed concrete (OPC) is not affected by type of curing such as in tap water, seawater, and air curing. 3. In general, elastic modulus of seawater mixed concrete and fly ash concrete cured in seawater or tap water is slightly larger than tap water mixed.

However, seawater mixed concrete cured in air was significantly increased compared with tap water mixed. 4. Seawater mixed concrete with or without fly ash decreased the pore volume of concrete at 28 days compared with tap water mixed, for tap water curing, seawater curing, and air curing. Meanwhile, porosity of seawater mixed with or without fly ash for tap water curing and seawater curing is nearly same. 5. Compressive strength of seawater mixed and tap water mixed concrete with or without fly ash in water curing (seawater and tap water) are influenced by its porosity.

6. The carbonation depth of seawater mixed concrete with or without fly ash is decreased compared with tap water mixed concrete. Replacement of fly ash increased the carbonation rate of concrete mixed with seawater and tap water. 7. The depth of carbonation of seawater mixed and tap water mixed concrete with and without fly ash had linear relationship with the square root of exposure duration in the accelerated carbonation test and it is not affected by mixing water and mix proportion of concrete. 8.

Relation between 28 days \square compressive strength and carbonation coefficient was clearly found and the compressive strength at 28 days can be used as an indicator to predict carbonation coefficient of seawater mixed and tap water mixed concrete and fly ash concrete. 9. Compressive strength and carbonation coefficient of seawater mixed and tap water mixed concrete at 28 days with or without fly ash may be controlled by its porosity. Acknowledgement The first author would like to express his gratitude to Directorate General of Higher Education, Ministry of Education and Culture of Indonesian government for their financial support during study in Kyushu University. References 1) P. Kumar Mehta and Paulo J.M.

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