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# **Properties and Application of Concrete Made with**

## Sea Water and Un-washed Sea Sand

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### ABSTRACT

We developed high-density and hard concrete using sea water and/or unwashed sea sand. The internal organizations of that concrete was denser compared with normal concrete, and it was clear that the water-tightness, early strength, and long-term strength of sea water and unwashed sea sand concrete were increased by adding mixture materials such as ground granulated blast-furnace slag, silica fume, fly ash and special admixture containing calcium nitrate. Reinforced concrete structures that used a non-corrosive reinforcing bar were durable in the long term. Sea water and unwashed sea sand concrete construction could be used on remote islands or on the coast to reduce  $CO_2$  emission and concrete and the examination about application to the concrete structures.

Keywords. Sea Water, Sea Sand, Chloride Ion, Ground Granulated Blast-furnace Slag, Calcium Nitrate

### **INTRODUCTION**

This paper describes the development of "concrete made with sea water and unwashed sea sand". A combination of sea water, unwashed sea sand, normal portland cement (OPC), ground-granulated blast-furnace slag (GGBS), fly ash (FA), silica fume (SF), and a special chemical admixture containing calcium nitrate (CN) was adopted to densify concrete. This concrete is hereafter referred to as "sea water and unwashed sea sand concrete"

Though the early strength of concrete containing sea water as mixing water is reported to be slightly higher in some of previous studies, the properties of concrete made using sea water and unwashed sea sand and containing a large amount of chloride ions and other ions derived from sea water have not been thoroughly clarified.

From the aspect of preventing concrete deterioration due to reinforcing steel corrosion, the current domestic standards specify the maximum chloride ion content of concrete at the time of placing. Also, the use of sea water and unwashed sea sand for reinforced concrete structures is prohibited except for plain concrete with no additional reinforcement. However, non-corroding reinforcement has been developed in recent years including epoxy-coated steel bars, stainless steel bars, and carbon fiber rods. These are proven to ensure durability of reinforced concrete even in the presence of a high concentration of chloride ions.

This technique not only improves the performance of concrete but also shortens the material transportation process and reduces the cost and  $CO_2$  emissions from construction work by effective use of sea water and sea sand when producing concrete in a region where fresh water and land sand are not readily available, such as isolated islands and coastal areas.

This paper reports on the physical properties of concrete made with sea water and unwashed sea sand, evaluation of reinforcement corrosion and deterioration, results of a trial calculation for  $CO_2$  emissions and construction cost in a project using this concrete on an isolated island, and methods of its application to reinforced concrete structures.

## MATERIALS AND METHODS OF EVALUATION TESTS

**Materials and Mixture Proportions.** Table 1 gives the materials of concrete used for the tests. Tap water or sea water was used for mixing. OPC, GGBS, FA, and SF were used as binders. A special chemical admixture containing calcium nitrate as a major component (CN) was also used to increase the strength and denseness of concrete.

Table 2 gives the mixture proportions of mortar. The water-binder ratio (W/B) and fine aggregate-binder ratio (S/C) were 0.5 and 3.0, respectively, for mixtures made with (a) tap water, (b) sea water, and (c) sea water + CN. The compositions of binders given in Table 3 were examined for each of the three water types. The dosage of CN was counted as part of the unit water content. Note that, for mortar testing, the total chloride ion content of mortar was  $4.6 \text{ kg/m}^3$  when using land sand as fine aggregate and sea water as mixing water.

Material.	Description	Code	Specification
Water	Tap Water	WT	from Bureau of Waterworks Tokyo
(W)	Sea Water	WS	from Suruga Bay in Shizuoka, Cl <sup>-</sup> Concentration : 1.83%
Binder (B)	Ordinary Portland Cement	OPC	Density : 3.16g/cm <sup>3</sup>
	Ground-Granulated Blast-Furnace Slug	GGBS	Density : 2.89g/cm <sup>3</sup>
	Fly Ash	FA	Density : $2.17$ g/cm <sup>3</sup>
	Silica Fume	SF	Density : $2.20$ g/cm <sup>3</sup>
Fine Aggregate	Land Sand	S	Density : $2.62 \text{g/cm}^3$
Coarse Aggregate	se Aggregate Crushed Stone		Density : $2.65 \text{g/cm}^3$
	Water Reducer	AE	Density : $1.05 \text{g/cm}^3$
Admixture	Special Admixture	CN	Containing Calcium Nitrate, Density : 1.29g/cm <sup>3</sup>

Table 1. Materials of Concrete

Table 4 gives the mixture proportions of concrete and fresh concrete test results. The binder composition was 50% OPC and 50% GGBS, and the water-binder ratio was 50% for all mixtures. Tests were conducted using four cases of mixture materials: (a) tap water, (b) sea water, (c) sea water + CN, and (d) sea water + CN + SF. Assuming that the NaCl content of unwashed sea sand to be 0.3%, NaCl was added to attain an equivalent chloride ion content (1.5 kg/m<sup>3</sup>). The total chloride ion content of concrete for these tests was 4.7 kg/m<sup>3</sup>.

Table 3. Compositions of Binders

Case W/B		Unit Content (kg/m <sup>3</sup> )					Case	Blended Content (%)				
	W/B	S/B	W					Case	OPC	GGBS	FA	SF
			WT	WS	В	S	CN	B30	70.0	30.0	0	0
(a)		.5 3.0	255 0 510 1518 0		B50	50.0	50.0	0	0			
(b)	0.5		0	255	510	1518	0	B70	30.0	70.0	0	0
(c)			0	242	510	1518	17	F20	80.0	0	20.0	0
	1							B50SF15	42.5	42.5	0	15.0
								F20SF15	68.0	0	17.0	15.0

Table 4. Mixture Proportions and Properties of Concrete

	W/D	,	Unit Content (kg/m <sup>3</sup> )									Properties of Fresh Concrete	
	W/B (%)	s/a (%)	W		В							Slump	Air
			WT	WS	OPC	GGBS	SF	S	G	AE	CN	(cm)	Content (%)
(a) Tap Water	- 50.0	45.0	170	0	170	170	0	794	985	0.85	0	16.5	4.7
(b) Sea Water		45.0	0	170	170	170	0	794	985	0.85	0	15.0	3.8
(c) Sea Water +AN		45.0	0	157	170	170	0	794	985	0.85	17	14.0	4.0
(d) Sea Water +SF+AN		47.5	0	157	152	152	34	782	985	0.85	17	17.5	3.3

**Test Items and Methods.** Table 5 gives the test items and methods. Compression tests were conducted at ages of 7, 28, and 91 days. Water permeability tests for concrete were conducted on cylinders 100 mm in diameter and 200 mm in length. The permeability coefficient was determined from the permeation depth by the input method (water pressure: 1.0 MPa, 48 hour) using specimens standard-cured up to an age of 28 days. Hydration products were analyzed by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD).

The degree of corrosion and deterioration of reinforcement were examined after repeat testing of 33 cycles specified in JCI SC2 between autoclave curing at 180°C under 10 atm for 8 hour and ordinary pressure/temperature, which corresponds to 100 years in a marine environment.

Test item	Method	Mortar	Concrete
Compressive Strength	JIS A 1108	0	0
Water Permeability	Water Permeability (Input Method)		0
Hydration Products Analysis	Scanning Electron Microscopy (SEM)	0	
	X-Ray Diffraction (XRD)	0	
Resistance for Freezing and Thawing	JIS A 1148		0
Time of Setting	JIS A 6204		0
Length Change Due to Drying Shrinkage	JIS A 1129-1 (Method with Comparator)		0
Corrosion of Reinforcement	JCI SC2(Autoclaving Method)		0

Table 5. Test Items and Methods

### PROPERTIES OF SEA WATER AND UNWASHED SEA SAND CONCRETE

**Compressive Strength.** Figures 1, 2, and 3 show the compressive strength of mortar at 7, 28, and 91 days, respectively. When GGBS was used to a replacement ratio of 30% to 70%, the compressive strength with sea water is 30% to 60% higher at 7 days and 3% to 20% higher at 28 days than with tap water. At 91 days, the strength with sea water is approximately 15% higher when the replacement ratio is 30%, but no significant strength gains due to sea water are appreciable when the replacement ratio exceeds 50%. When FA is used (replacement ratio: 20%), the compressive strength with sea water is 14%, 6%, and 6% higher than with tap water at 7, 28, and 91 days, respectively. When SF is used (replacement ratio: 15%), the combinations with GGBS and FA lead to compressive strengths 37% and 18% higher, respectively, with sea water than with tap water at 7 days. At 28 days, the strength gains due to sea water are 14% and 17% in combination with GGBS and FA, respectively. At 91 days, the strength gains due to sea water are 3% and around 2% with GGBS and FA, respectively.

In the presence of either GGBS or FA, the use of sea water as mixing water increases the strength up to 28 days, but the strength gains are not significant at 91 days.

The compressive strength of mortar mixed using sea water and containing CN was then investigated. In the presence of GGBS, the strength with sea water at 7, 28, and 91 days was around 1.5 to 2.5 times, 1.5 times, and 1.2 times, respectively, the strength with tap water. In the presence of FA, the strength with sea water at 28 and 91 days was approximately 20% and 30%, respectively, higher than with tap water. When SF is additionally used, the strength with GGBS and FA was approximately 30% and 20%, respectively, higher with sea water than with tap water both at 28 and 91 days.

Accordingly, when GGBS and FA are used as binders, the use of sea water and addition of CN and SF are found to significantly increase the early strength (7 days) and moderately increase the long-term strength (91 days) in all cases. This is presumably because the addition of CN to concrete containing sea water increases the OH concentration in the pore solution, intensifying the alkali stimulus to GGBS and FA, thereby accelerating hydration.



Figure 3. Compressive Strength of Mortar (Age 91days)

Figure 4 shows changes in the compressive strength of concrete in which 50% of the binder is replaced with GGBS. At 7 days, the compressive strength with sea water is approximately 60% higher than that with tap water. When CN and SF are added, the strength is approximately 70% higher. At 28 days, the strength with sea water is approximately 30% higher than that with tap water. When CN and SF are added, the strength gain is approximately 60%. At 91 days, the strength with sea water is not significantly high, but the addition of CN and SF leads to an increase of approximately 20% when compared with the strength with tap water.

It has conventionally been known that the inclusion of chlorides in concrete made using OPC increases early strength but long-term strength gains are limited. Similar tendencies were confirmed in the present tests as well. However, the use of sea water, unwashed sea sand, GGBS, FA, SF, and CN in combination was found to accelerate hydration of GGBS and pozzolans, increasing not only early strength but also long-term strength.



Figure 4. Compressive Strength of Concrete

**Setting Times.** Figure 5 shows the results of concrete setting tests. The initial and final setting times of concrete mixed using sea water were 1 h 30 min and 2 h 15 min, respectively, shorter than those with tap water. Also, the use of CN scarcely affected the setting times.



Figure 5. Time of Setting by Penetration Resistance

**Watertightness.** Figure 6 shows the permeability coefficient of concrete made using 50% OPC and 50% GGBS as the binder. Whereas the permeability coefficient of concrete mixed using tap water is  $3.3 \times 10^{-12}$  m/sec, those of concrete mixed using seawater, such concrete containing AN, and such concrete containing both AN and SF are approximately 1/2, 1/4, and 1/70, respectively. Thus the use of seawater, AN, and SF in combination is found to significantly improve the watertightness of concrete.

Photo 1 shows SEM images of mortars comparing microstructures of concrete mixed using tap water and concrete made with sea water as mixing water, CN, and SF. Many needle crystals of ettringite are formed in the pores of concrete mixed using sea water. It is inferred that these crystals filling large voids densify the microstructure.

Figure 7 shows the XRD intensity of ettringite in concrete made using 50% OPC and 50% GGBS as the binder. Similarly to the observation results of SEM, the ettringite formation in concrete using sea water is approximately 30% greater than in concrete using tap water. The increase in ettringite formation is found to be approximately 120% with sea water and CN. While ettringite is also formed in normal concrete, the increased ettringite formation in concrete containing sea water and CN can be attributed to chemical reaction between sulfate ions abundant in sea water and components of the binder containing calcium and aluminum.







(a) Tap Water (b) Sea Water + CN + SF Photo 1. SEM Images of Mortars



Figure 7. XRD Intencity of Ettringite in Concrete

**Resistance to Freezing and Thawing Action.** Figures 8 and 9 show changes in the relative dynamic modulus and mass loss ratio, respectively, through freezing and thawing cycles. The total chloride ion content in these tests was 3.1 kg/m<sup>3</sup>, which was derived from sea water. Specimens with an air content of over 3.1 kg/m<sup>3</sup> achieve a relative dynamic modulus of not less than 85% and marginal mass loss after 300 cycles regardless of mixture proportions, showing no deterioration due to cyclic freezing and thawing. It is therefore considered that, similarly to normal concrete, resistance to freezing and thawing action can be ensured by setting the air content at 3.5% also for concrete containing sea water as mixing water.



Figure 8. Changes in Relative Dynamic Modulus



**Drying Shrinkage.** Figure 10 shows the length change ratio due to drying shrinkage. The total chloride ion content of concrete in these tests was 3.1 kg/m3, which was derived from sea water. The autogenous shrinkage strain of concrete mixed using sea water tends to be slightly larger than that of concrete with tap water. However, the drying shrinkage strain was slightly smaller than that of concrete with tap water by a margin of  $500 \times 10^{-6}$  to  $700 \times 10^{-6}$  in all cases.

**Corrosion and Deterioration of Reinforcement.** Photo 2 shows the deterioration state of epoxy-coated steel reinforcement, carbon fiber rods, and normal steel reinforcement after cyclic acceleration tests between autoclave conditions and ordinary pressure/temperature. At the end of 33 cycles corresponding to 100 years in a marine environment, the surfaces of normal steel bars were entirely corroded, but no corrosion or deterioration was observed on epoxy-coated steel bars or carbon fiber rods.



Figure 10. Length Change Ratio Due to Drying Shrinkage



(a) Epoxy Coated Steel

(b) Carbon Fiber Rod

(c) Normal Steel

Photo 2. Result of Corrosion Test by Autoclaving Method

# APPLICATION OF SEA WATER AND UNWASHED SEA SAND CONCRETE TO STRUCTURES

**Production Method.** Sea water and unwashed sea sand concrete can be produced in a manner similar to normal concrete by constructing a concrete plant near the sea as shown in Fig. 11. Sea water to be used as mixing water should be pumped up from the sea and filtered to remove foreign matter. Sea sand should be taken from the sea bottom or shore and used as it is without being rinsed with water to remove salt. Supplementary cementitious materials and chemical admixtures should be added to the mixer of the plant at the time of mixing, to produce sea water and unwashed sea sand concrete. The resulting concrete can be conveyed using normal agitating trucks and mobile pumps.

When using sea water and unwashed sea sand concrete for reinforced concrete structures, corrosion-resistant reinforcement should be used. These include epoxy-coated steel bars, carbon fiber rods, stainless-steel bars, and galvanized steel bars. Also, metal materials to be embedded in concrete, such as separators and embedded metal fittings should preferably be coated with a corrosion-resistant material or made of ceramic, etc.

**Evaluation of Cost and CO<sub>2</sub> Emissions.** The construction cost and CO<sub>2</sub> emissions when using sea water and unwashed sea sand concrete were estimated based on a model case of retaining wall construction (amount of concrete:  $1,000 \text{ m}^3$ , design service life: 100 years)

in a marine environment on an isolated island 100 km off the coast of the mainland, where pure water and land sand are scarcely available. The values of specific  $CO_2$  emissions were adopted from JSCE's recommendations for verification of environmental performance of concrete structures (draft). Figure 12 compares Plan A in which concrete is produced using fresh water and land sand conveyed on a transport boat from the mainland and Plan B in which concrete is produced using sea water and sea sand available on the island. Although a certain amount of pure water, also in plan B, is to be conveyed in order to wash the inside of a plant, this is taken into consideration in the case of cost and  $CO_2$  emissions calculation. In both plans, concrete is to be produced using a simple plant constructed at the job site, and epoxy-coated steel bars are to be used as reinforcement.

The trial calculation has demonstrated that the construction cost using sea water and unwashed sea sand concrete is approximately 6% and 10% less with and without reinforcement, respectively, than that of the case where fresh water and land sand are conveyed on a transport boat from the mainland. Also, CO<sub>2</sub> emissions from construction using sea water and unwashed sea sand concrete are approximately 40% smaller than those of construction in which fresh water and land sand are conveyed from the mainland.

Accordingly, sea water and unwashed sea sand concrete not only improves the quality and durability of the structure, but also can contribute to reductions in the construction cost and  $CO_2$  emissions when used for construction in regions where material availability is limited.



Figure 11. Produce Method of Sea Water and Unwashed Sea Sand Concrete



Figure 12. Comparison of Constructing Cost and CO<sub>2</sub> Emission (in the Case of Using Sea Water and Unwashed Sea Sand Concrete)

#### CONCLUSIONS

The properties and use effect of sea water and unwashed sea sand concrete (concrete and mortar made using a combination of sea water, unwashed sea sand, fly ash, silica fume, and calcium nitrate) were investigated, and the following were found:

(1) Early strength of sea water and unwashed sea sand concrete (total chloride ion content: around  $4.5 \text{ kg/m}^3$ ) is high, and long-term strength is also retained at a high level.

(2) The permeability coefficient of sea water and unwashed sea sand concrete (total chloride ion content: around 4.5 kg/m<sup>3</sup>) becomes small compared with that of concrete made using tap water, as a result of density of its microstructures.

(3) The resistance to freezing and thawing of sea water and unwashed sea sand concrete (total chloride ion content: around  $3.1 \text{ kg/m}^3$ ) can be ensured by setting an air content level of not less than 3.5 %.

(4) The drying shrinkage strain of sea water and unwashed sea sand concrete (total chloride ion content:  $3.1 \text{ kg/m}^3$ ) is smaller than that of concrete made using tap water.

(5) For a construction project on an isolated island, the use of sea water and unwashed sea sand contributes to 'production for local consumption,' reduces the construction and material transportation cost, and reduces the  $CO_2$  emissions.

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