

Properties of hydrated hardened solids made of iron and steel slag exposed in sea area for 5 years

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ABSTRACT

Hydrated hardened solids of iron and steel slag exposed in sea area for 5 years were examined. Both test materials exposed in splash zone and tidal zone have their compressive strength of over 40 N/mm², which is over 50% larger than samples after standard curing for 4 weeks. The average neutralization depths were less than 1 mm, and the neutralization rate coefficients were smaller than that of ordinary portland cement concrete and slag cement concrete with effective water-binder ratio of 66-70%. The concentrations of chlorine ions were less than 1.2 kg/m³, that is a critical concentration of steel corrosion, except 2 centimeters from surface. The apparent Cl diffusion coefficients were less than 0.1cm²/year, which is lower than one-tenth compared to that of ordinary portland cement concrete and slag cement concrete. Hydrated hardened solids have the same or greater long-term stability than ordinary portland cement concrete or slag cement concrete.

Keywords. Hydrated hardened solids, uniaxial compressive strength, neutralization rate coefficient, apparent Cl diffusion coefficient, sea area

INTRODUCTION

It is becoming more and more important to reduce CO₂ emissions and recycle industry by-products for sustainability. Therefore hydrated hardened solids of iron and steel slag were developed as a new material for civil engineering and construction in 1999. The manufacturing process of this material is shown schematically in [Figure 1](#). This material consists of steelmaking slag as an aggregate, GGBFS as a binder, and the manufacturing

process is similar to that of ordinary cement concrete products. This technology makes it possible to build structures with a small quantity of cement, thereby reducing CO₂ emissions associated with cement manufacturing and avoiding environmental destruction due to mining of genuine stone. It has various desirable features such as low alkali elution and excellent biofouling capability, while providing the same strength performance as ordinary concrete, higher density, and excellent wear resistance. However, in addition to these facts, the long-term changes in the physical and chemical properties such as neutralization should be clarified. Particularly we focused on its long-term stability in sea area, and so we examined hydrated hardened solids exposed in splash zone and tidal zone for 5 years.

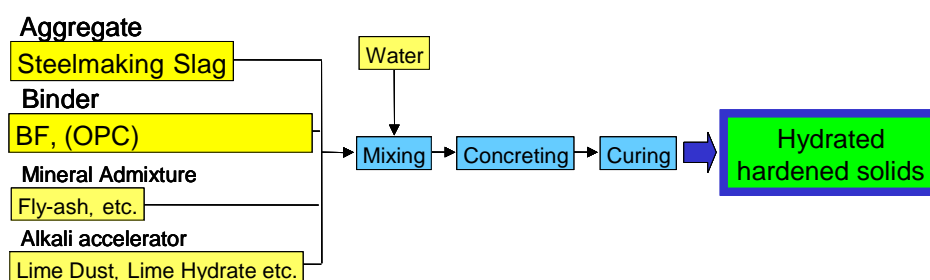


Figure 1. Manufacturing process of hydrated hardened solids

EXPERIMENTAL OVERVIEW

Materials and mixture proportions. The mixture proportions of samples were listed in Table 1. Hydrated hardened solids (No. HHS-1) contains eighty-five percent of ground granulated blast furnace slag (BF, Density: 2.88g/cm³) and fifteen percent of ordinary portland cement (OPC, Density: 3.15g/cm³) as binders. And it also contains fly ash (Density: 2.27g/cm³) as a mineral admixture, steelmaking slag (0-5mm, Density: 3.20g/cm³) (5-25mm, Density: 3.11g/cm³) as a fine aggregate and a coarse aggregate. Slag cement concrete (No. BB) was also cast. Although it has different Water/Binder ratio, we use this sample by way of comparison. Slag cement (Density: 3.04g/cm³) contains forty-one percent of BF and fifty-nine percent of OPC. As a fine aggregate, sand (Density: 2.59g/cm³) is used, and as a coarse aggregate, stone (Density: 2.70g/cm³) is used.

Table 1. Mixture proportions of hydrated hardened solids and concrete

No.	Date of casting	Unit content(kg/m ³)									(kg/m ³)	
		W	slag cement* ₁	BF* ₂	OPC	fly ash	steelmaking slag		sand	stone	Admixture	
							0-5mm	5-20mm			High range	normal
HHS-1	2007/1/26	183	0	297	53	134	902	1008	0	0	4.83	
BB	2007/1/31	160	276	0	0	0	0	0	842	1023	0	0.69

*1 slag cement: BF 59%, OPC 41% (ratio by weight)

*2 BF: Ground granulated blast furnace slag powder

Sample size and exposure conditions. Cylindrical specimens of $\phi 100 \times 200$ mm were used for exposure test. After casting, the specimens were cured in water for more than 28 days, and then were exposed in test area from March 2007. The exposure conditions of the samples are listed in **Table 2**. The samples were exposed in exposure test area (Kanagawa Pref., Japan). The exposure environments were the splash zone and tidal zone. Three specimens were recovered from each environment in March 2012 after exposure for 5.0 years (**Photo 1**). For comparison, the same samples were cured in standard condition and uniaxial compressive strength was examined.

Examination items and methods. One of the three samples was cut and divided into two parts (**Figure 2**). The lower part ($\phi 100 \times 130$ mm) of the sample and other two samples ($\phi 100 \times 200$ mm) were used for measurement of uniaxial compressive strength. The remaining upper part ($\phi 100 \times 70$ mm) was cut vertically and divided into two parts (**Figure 2**). Each part is used for measurement of neutralization depth using phenolphthalein reaction, an elemental distribution using EPMA, respectively.

Table 2. Exposure conditions

exposure area	environmental compartment
Port and Airport Research Institute exposure test area, Kanagawa prefecture, Japan average temperature:15.6°C, annual rainfall:1500mm	Splash zone
	Tidal zone



Photo 1. Specimens after 5 years exposure (HHS-1, left: splash zone, right: tidal zone)

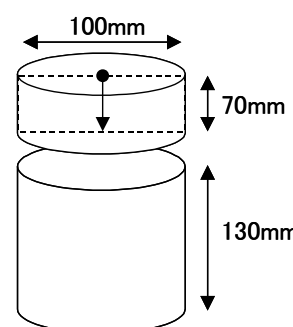


Figure 2. Schematic image of cut plane

RESULT AND DISCUSSION

Uniaxial compressive strength. The measurement results of uniaxial compressive strength of HHS-1 and BB are shown in **Figure 3**. In both the splash and tidal zones, compressive strength of HHS-1 and BB increases with exposure time. The HHS-1 samples in splash zone have lower strength than BB after 5 years. The reason why the strength of BB

is higher than that of HHS-1, those have same strength at 28 days aging, is based of binding material's composition. According to "Manuals for Steel Slag Hydrated Matrix", the following experimental equation is used as the index of uniaxial compressive strength at 28 days aging.

$$(\text{strength index})=(2\text{OPC}+\text{BF}+0.35\text{FA})/\text{W} \quad (1)$$

In this equation, FA indicates fly ash, and quantity per unit volume (kg/m^3) is used. The strength index of HHS-1 is 2.46, and that of BB is 3.09. The strength index of BB is higher than that of HHS-1, so the strength of BB cured in water shows a greater upward tendency than that of HHS-1 cured in water. This is considered to be a reason why the strength of BB is higher than that of HHS-1 in the splash zone.

On the other hand, difference of strength becomes smaller in tidal zone. The strength of HHS-1 in splash zone and tidal zone are almost same. This indicates HHS-1 has higher resistance than BB against seawater. It is assumed that ground granulated blast furnace slag affects such higher resistance against seawater.

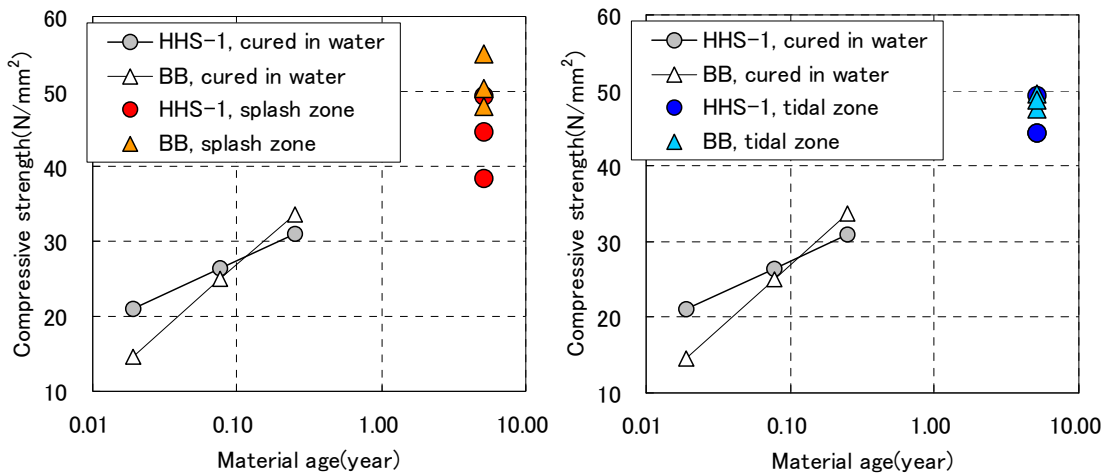


Figure 3. Changes of uniaxial compressive strength (left: splash zone, right: tidal zone)

Neutralization depth. Neutralization in cement concrete or in hydrated hardened solids does not directly cause strength decrease, but when steel reinforcing rebar are embedded in the material, neutralization causes rebar corrosion, and this has a huge effect on material strength. The measurement results of neutralization depth are shown in Table 3. Neutralization depths of HHS-1 both in splash zone and tidal zone are smaller than that of BB. Neutralization occurs in consequence of carbon dioxide in the atmosphere and carbonate

ions in seawater, and the neutralization depth in the splash zone is deeper than that in tidal zone generally. In this study, the same tendency was confirmed.

The neutralization rate coefficient was calculated from the measured results. The neutralization depth is expressed by the following equation, and is proportional to the square root of time and the neutralization rate coefficient.

$$L = a\sqrt{t} \quad (2)$$

L : neutralization depth (mm)

a : neutralization rate coefficient (mm/ $\sqrt{\text{year}}$)

t : time (year)

Table 3. Neutralization depth and neutralization rate coefficient

zone	Sample	number of measurement	neutralization depth (mm)			Neutralization rate coefficient (mm/ $\sqrt{\text{year}}$)
			Min	Max	Ave	
Splash	HHS-1	10	0.0	3.0	0.75	0.34
	BB	10	0.0	4.5	0.8	0.36
Tidal	HHS-1	10	0.0	1.0	0.5	0.22
	BB	10	0.0	3.5	0.7	0.31

The calculated rate coefficient was from 0.2 to 0.4 mm/ $\sqrt{\text{year}}$. Neutralization has strong relationship with the effective water-binder ratio. Even if the water-binder ratio were the same, slag cement concrete (BB), which contains more GGBFS than ordinary Portland cement concrete (N), would have lower neutralization resistance, because BB contains less lime than N and thus is disadvantageous for neutralization. According to “Standard Specification for Concrete Structures-2007 (Design)”, the effective water-binder ratio expressed by the following experimental equation is used to estimate the neutralization rate coefficient.

$$W/B^* = W/(OPC+0.7BF) \quad (3)$$

B^* : effective binder quantity per unit volume

The neutralization rate coefficient of HHS-1 was compared with that of ordinary concrete (N and BB) using this factor. The results for the tidal zone are shown in [Figure 4](#). The estimated formula of N and BB proposed by Japan Society of Civil Engineers are also shown in [Figure 4](#). The neutralization rate coefficient of HHS-1 is smaller than that of BB (this study) and that of reference data (N and BB).

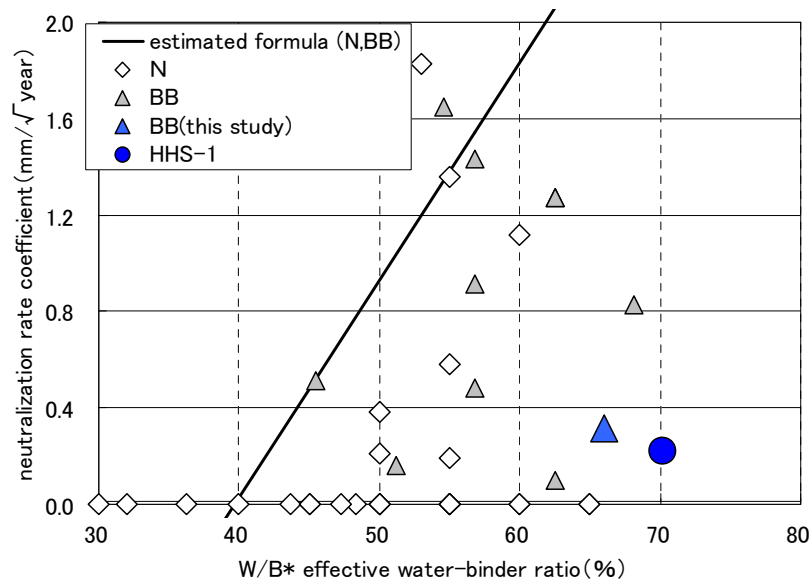


Figure 4. Neutralization rate coefficient compared with ordinary concrete (tidal zone)

Elemental distribution (EPMA). In addition to neutralization, chlorine penetration causes rebar corrosion. The results of EPMA mapping (Cl) of the tidal zone sample are shown in Figure 5. Higher chlorine ion area is found near the surface, which indicates chlorine ions in seawater penetrate the sample interior from the surface. The chlorine penetration depth of HHS-1 is smaller than that of BB. The same results were confirmed with the undersea zone sample.

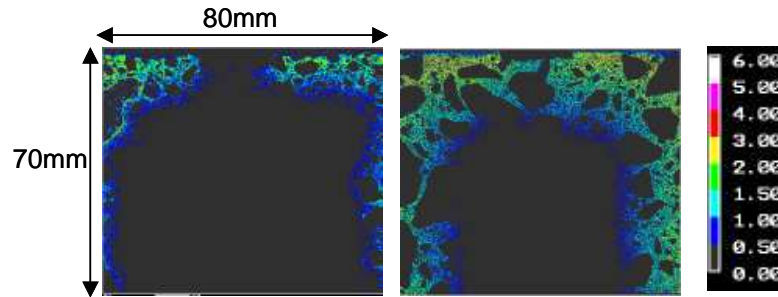


Figure 5. Cl mapping (left: HHS-1 tidal zone, right: BB tidal zone)

The crosswise average Cl concentration in the depth direction was calculated in the same range as in the EPMA mapping. The results are shown in Figure 6. Aggregate is excluded from the calculation, and the threshold level of chlorine ion is considered to be 1.2kg/m^3 in this paper, based on steel rebar corrosion reports.

Both in the splash zone and the tidal zone exposure, the chlorine ion concentration of HHS-1 in the range over two centimetres in depth is less than 1.2kg/m^3 . And in this study, splash zone and tidal zones is similar from the viewpoint of chlorine penetration.

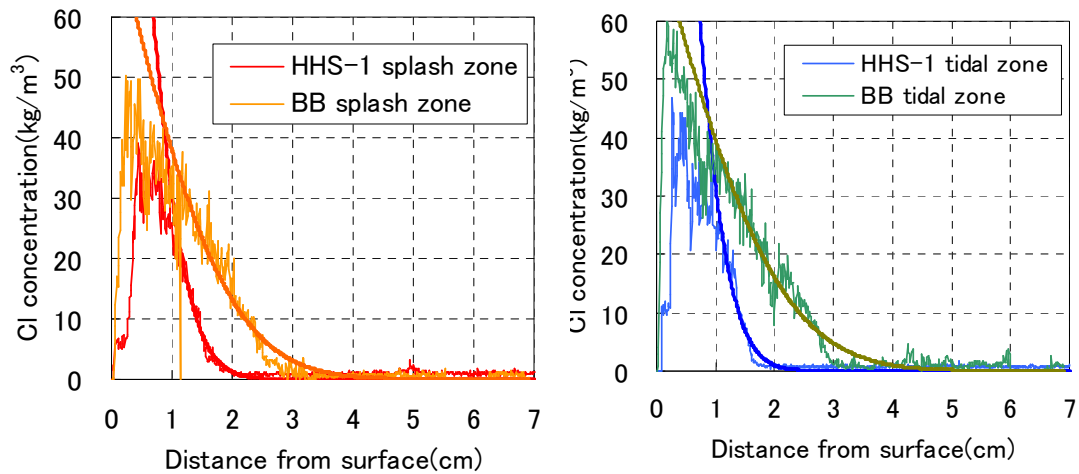


Figure 6. Cl concentration by EPMA line analysis (left: splash zone, right: tidal zone)

To compare with earlier reports, the apparent Cl diffusion coefficient was calculated. The chlorine concentration of concrete exposed in sea area is expressed by the following diffusion equation.

$$C(x,t) = C_0 \left\{ 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right\} \quad (4)$$

$C(x,t)$: Cl concentration (kg/m³)

C_0 : surface Cl concentration (kg/m³)

D : apparent diffusive coefficient (cm²/year)

x : distance from surface (cm)

t : time after exposure (year)

erf : error function

Coefficient D indicates an apparent diffusion coefficient. The Cl diffusion coefficient D can be calculated by fitting the observed results into this equation. Data from 0 to 1 centimetres in depth were excluded from fitting, since this area might be affected by Cl reduction caused by neutralization. The calculated values obtained by fitting are also shown as solid lines in Figure 6. The Cl diffusion coefficients obtained by fitting are listed in Table 4.

Table 4. Calculated Cl diffusion coefficient

zone	Sample	Cl diffusion coefficient (cm ² /year)
Splash	HHS-1	0.055
	BB	0.213
Tidal	HHS-1	0.050
	BB	0.262

The calculated Cl diffusion coefficients in tidal zone are shown in Figure 7 in comparison with the values of cement concretes N and BB. The estimated formula of N and BB proposed by Japan Society of Civil Engineers are also shown in Figure 7. Both the Cl diffusion coefficient of HHS-1 and BB (this study) is almost one-tenth of N and BB in earlier reports. It is assumed that ground granulated blast furnace slag affects such higher resistance against Cl penetration.

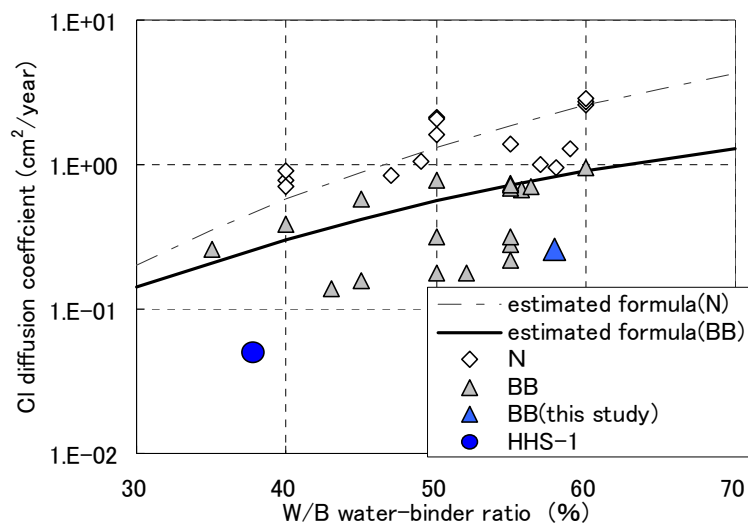


Figure 7. Cl diffusion coefficient compared with ordinary concrete (tidal zone)

CONCLUSION

Properties of hydrated hardened solids of iron and steel slag (HHS) exposed in sea area for 5 years was examined. Both in splash zone and tidal zone, the uniaxial compressive strength after 5 years of exposure were over 40 N/mm². The strengths of HSS-1 in splash zone and tidal zone were almost same level. And in the tidal zone, it is same level as BB concrete, although the strength index of HHS is smaller than that of BB. The average neutralization depths were under 1 mm, and the neutralization rate coefficients were smaller than that of BB concrete. The concentrations of chlorine ions were less than 1.2 kg/m³, that is a critical concentration of steel corrosion, except 2 centimeters from surface. The apparent Cl diffusion coefficients were less than 0.1cm²/year, and lower than one-tenth compared to that of ordinary portland cement concrete and slag cement concrete. Hydrated hardened solids have the same or greater long-term stability than ordinary portland cement concrete or slag cement concrete for sea area construction materials.

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