

## Study on Concrete Deterioration and Deterioration Indicators in Marine Environments

Toru Yamaji<sup>1</sup>, Yoshikazu Akira<sup>2</sup>, Hidenori Hamada<sup>3</sup>, and Kazuo Yamada<sup>4</sup>

<sup>1</sup>*Port and Airport Research Institute, Japan*

*3-1-1, Nagase, Yokosuka, Kanagawa, yamaji-t@pari.go.jp*

<sup>2</sup>*Toyo Construction (Former Port and Airport Research Institute), Japan*  
*1033-1, Ukeryo, Miho, Inashiki-gun, Ibaraki, akira-yoshikazu@toyo-const.co.jp*

<sup>3</sup>*Kyushu University, Japan*

*744, Moto-oka, Nishi-ku, Fukuoka, h-hamada@doc.kyushu-u.ac.jp*

<sup>4</sup>*National Institutes for Environmental Studies, Japan*

*16-2, Onogawa, Tsukuba, Ibaraki, yamada.kazuo@nies.go.jp*

### ABSTRACT

In order to investigate the deterioration of concrete in marine environments, both concrete cores sampled from existing structures and test specimens exposed in an outdoor pool of natural seawater are used. These specimens were examined using the Vickers hardness test and EPMA (Electron Probe Micro Analyzer). The following behaviors were observed:

- 1) The penetration depth of  $Mg^{2+}$  was correlated with both the neutralization depth and the depth of  $SO_4^{2-}$  penetration.
- 2) Deteriorated areas in concrete specimens determined by Vickers hardness were correlated with the penetration depth of  $Mg^{2+}$ . One reason for this deterioration is considered to be the phase change of C-S-H (Calcium silicate hydrate) to M-S-H (Magnesium silicate hydrate), which has a lower strength than C-S-H.
- 3) The penetration depth of  $Mg^{2+}$  can be an indicator of concrete deterioration progress in marine environments.

**Keywords:** marine environments, deterioration, Vickers hardness, neutralization depth, penetration depth of magnesium ions

### INTRODUCTION

The main factor of the deterioration of concrete in marine environments was considered to be sulfate attack. Sulfate attack was considered to be caused by  $SO_4^{2-}$ ,  $Mg^{2+}$ , etc. in seawater. However, the concentration of ions, such as  $SO_4^{2-}$ ,  $Mg^{2+}$ , etc., in seawater is not high compared with typical environments such as desert or delta areas, therefore the rate of deterioration is relatively slow. As a result, it takes a long time to evaluate the durability of

concrete in actual marine environments. Therefore, the deterioration rate of concrete in marine environments is not clear, and the estimation method of the rate is not established.

In this study, in order to understand the actual condition of concrete deterioration in marine environments, various tests were carried out on both concrete cores sampled from existing structures and test specimens exposed in an outdoor pool of natural seawater for a prolonged period.

Deterioration due to sulphate attack is considered to progress gradually from the surface of concrete exposed to seawater. Therefore, the Vickers hardness test was carried out to investigate the depth of deterioration from the surface. Decrease in hardness is assumed deterioration. Here, the range of deterioration from the surface is defined as the 'deterioration depth'.

If a correlation between the deterioration depth by Vickers hardness and the penetration depth of some element, for example  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ , etc., is clearly recognized, the penetration depth is considered to be an indicator of concrete deterioration. In order to investigate the

**Table 1. Summary of sampled concrete cores**

Port (Structure)	Member	Age (year)	Exposure environment	Distance from H.W.L.(m)	Test results				
					$\sigma$ ( $\text{N}/\text{mm}^2$ )	$y_n$ (mm)	Result of EPMA(mm)		
							Mg	$S_{\max}$	Ca
A (Wharf)	Slab	39	Splash	1.15	-	0.0	-	-	-
				1.15	-	9.6	-	-	-
	Beam			0.68	41.2	3.9	-	-	-
				0.89	-	2.1	-	-	-
				0.30	-	1.1	-	-	-
				0.69	-	0.0	-	-	-
B (Wharf)	Slab	35	Splash	1.35	-	3.5	-	2.0	5.5
				1.35	-	2.5	-	-	-
	Beam			0.76	31.8	4.0	-	-	-
				0.65	-	2.0	3.8	5.9	26.4
C (Wharf)	Slab	40	Splash	0.90	-	5.0	4.5	1.1	16.4
	Beam			0.17	42.8	-	-	4.4	7.6
D (Wharf)	Slab	19	Splash	1.00	-	2.5	-	1.4	1.3
				1.00	-	3.5	-	-	-
	Beam			0.39	41.0	3.0	4.5	1.2	16.4
				0.39	-	-	-	2.1	5.6
E (Wharf)	Slab	21	Splash	0.51	-	6.8	-	-	-
				0.51	-	6.7	-	-	-
	Beam			0.16	-	10.0	-	-	-
				0.16	-	10.2	-	-	-
	Tidal		-0.14	38.4	6.1	-	-	-	
			-0.14	-	10.2	-	-	-	
F (Breakwater)	Side wall	29	Splash	0.25	-	2.5	3.4	1.6	21.8
			Tidal	-0.05	-	1.6	1.9	2.0	21.8
G (Wharf)	Beam	39	Splash	0.55	-	6.5	5.1	10.4	10.5
				0.55	-	7.4	7.0	10.4	17.4
				0.55	-	4.8	-	-	-
				0.55	-	6.6	-	11.6	12.9

$\sigma$ : compressive strength,  $y_n$ : neutralization depth

concentration distribution of each element near the concrete surface, the EPMA (Electron Probe Micro Analyzer) was used. Also, the neutralization depth was measured.

Then, in order to identify the indicators of deterioration, correlation analysis of the deterioration depth and certain element involved in deterioration were performed. Trials of the deterioration prediction using the indicator of deterioration were also carried out.

## TEST SPECIMENS

**Sampled concrete core.** Concrete cores with a diameter of 50 or 100 mm were sampled from existing concrete structures at seven ports. Table 1 presents summary of sampled concrete cores. In the case of the upper deck of a wharf (Ports A, B, C, D, E, and G), core was sampled from the side of a beam and bottom of a slab. In the case of the breakwater (Port F), it was sampled from the side wall. The exposure environments were ‘tidal zone’ and ‘splash zone’. Here, the mixture proportions and materials used are unknown for all of the concrete cores. Detailed information about sampled core was described in elsewhere (Yamaji, 2010).

**Table 2. Materials used and mixture proportions of concrete specimens**

Case	Environment	Period (y)	Cement	W/C	Unit weight(kg/m <sup>3</sup> )				Test results						
									Compressive strength(N/mm <sup>2</sup> )		y <sub>n</sub> (mm)	Result of EPMA(mm)			y <sub>d</sub> (mm)
					28 days	After exposure	Mg	S <sub>max</sub>	Ca						
1	Tidal	15	N	0.45	162	360	738	1110	37.5	45.7	0	0.0	NC <sup>+</sup>	1.0	-
			BA	0.45	158	351	758	1094	38.1	41.9	0	2.2	1.8	5.0	-
			BB	0.45	160	355	736	1108	33.5	41.4	0	0.0	1.6	1.8	-
			BC	0.45	162	360	714	1120	29.5	37.1	0	1.8	5.2	5.4	-
			FB	0.45	158	351	738	1110	46.0	37.0	0	0.0	NC <sup>+</sup>	6.4	-
2	Tidal	12	N	0.50	178	356	786	1048	37.5	-	0	1.0	0.8	3.8	1.0
				0.55	178	324	798	1064	38.1	-	0	0.9	0.8	3.1	0.8
				0.60	178	293	810	1080	33.5	-	0	1.0	NC <sup>+</sup>	0.9	0.8
				0.60	157	262	661	1116	29.5	-	0	1.1	NC <sup>+</sup>	3.0	0.9
3	Submerged	30	N	0.53	153	290	740	1261	35.9	47 <sup>***</sup>	5	2.6	2.4	13.6	0.9
			N3'	0.55	158	290	734	1251	-	-	-	6.0	3.2	14.0	5.7
			HES	0.53	154	290	738	1258	41.7 <sup>*</sup>	46 <sup>***</sup>	5	5.0	5.0	11.2	4.7
			BB3	0.52	152	290	738	1258	37.2	46 <sup>***</sup>	2	3.8	3.2	5.6	5.1
			BB3'	0.55	159	290	729	1242	35.6	-	-	4.4	2.4	3.2	2.9
			AI	0.52	151	290	737	1256	41.9 <sup>**</sup>	35 <sup>***</sup>	2	0.0	0.8	1.4	1.0
4	Submerged	5	N4	0.50	160	320	798	1027	44.9	63.9	0	0.0	0.8	NC <sup>+</sup>	1.2
			BB4		154	308	800	1038	43.2	70.2	0	0.0	0.8	NC <sup>+</sup>	1.9
			E		158	316	780	1050	40.7	44.6	0	0.0	1.2	NC <sup>+</sup>	1.5
			EBB		158	316	774	1041	36.2	74.3	0	0.0	0.8	NC <sup>+</sup>	-
			E'		158	316	780	1050	35.6	40.4	0	0.0	1.4	NC <sup>+</sup>	-
			E'						35.6	41.9	0	0.0	2.0	NC <sup>+</sup>	-
	Tidal														
5	Tap water (Indoors)	5	N5	0.55	158	288	786	1094	50.4	57.7	-	0.0	NC <sup>+</sup>	NC <sup>+</sup>	0.5
	0.55			168	305	675	975	47.2	39.2	-	2.6	2.4	2.4	0.9	
								33.7	27.4	-	2.3	1.9	9.1	0.8	

y<sub>n</sub>: neutralization depth, y<sub>d</sub>: deterioration depth

\*7days, \*\*1day, \*\*\*60 × 60 × 60mm cube was cut out from specimen, +:Not clear

**Table 3. Cement types used in this study**

Name	Cement types	Notes
N	Normal Portland cement	
HES	High-early-strength Portland cement	
BA	Blast furnace slag cement Type A	Slag content: 5-30%
BB	Blast furnace slag cement Type B	Slag content: 30-60%
BC	Blast furnace slag cement Type C	Slag content: 60-70%
FB	Fly Ash cement Type B	Fly ash content: 10-20%
Al	Alumina cement	Main component: Calcium Aluminate
N3'	Normal Portland cement	The quantity of gypsum in N was increased with 2.0 mass % at SO <sub>3</sub> .
BB3'	Blast furnace slag cement Type B	The quantity of gypsum in BB was increased with 2.0 mass % at SO <sub>3</sub> .
E	Ecocement	Made of incinerator ash of general municipal waste
E'	Ecocement	Same type with E (different concrete placing time)
EBB	Ecocement with Blast furnace slag	Slag content: 50%

**Specimens.** Table 2 shows the materials used and mixture proportions of concrete. Specimens were divided into five cases. There were varying parameters among cement types, exposure environment, exposure period, etc. In Case 1, normal Portland cement (N), three types of Blast furnace slag cement (type A (BA), type B (BB), and type C (BC)), and fly ash cement type B were used. In Case 2 and Case 5, normal Portland cement was used. In Case 3, N, BB, high-early-strength Portland cement (HES), and Alumina cement (Al) were used. Here, N' and BB' are types of cement in which the quantity of gypsum in N and BB was increased (2.0 mass% at SO<sub>3</sub>). In Case 4, N, B, ecocement (E), and EBB which contains 50% of the blast furnace slag in 'E' were used. Here, N satisfied JIS R 5210, BA, BB, and BC satisfied JIS R 5211, FB satisfied JIS R 5213, and E satisfied JIS 5214, which is made of incinerator ash of general municipal waste as burning raw materials in more than half quantity. Table 3 shows the cement types used in this study.

Aggregate used was natural fine and coarse aggregate in Cases 1 - 4, and recycled fine and coarse aggregate in Case 5. The chemical admixture used was an AE water reducing agent. Detailed information has been described in Yamaji, 2010.

The specimens for Cases 1, 2, 3 and 4 were exposed to 'tidal zone' and 'submerged zone' environments in the facility (called a 'tidal pool') of the Port and Airport Research Institute. Natural seawater was automatically pumped into and drained out of the facility. The water level was changed twice per day.

The specimen for Case 5 was exposed to a standard curing condition in a) tap water in a room, and b) in natural seawater in a room. The water temperature was 20 °C.

## **MEASUREMENTS**

Following properties were evaluated in this study in order to clarify.

### (a) Compressive strength

The compressive strength was measured according to JIS A 1108.

### (b) Neutralization depth

The neutralization depth was measured according to JIS A 1152.

(c) EPMA (Electron Probe Micro Analyzer)

Using EPMA, the profiles of Ca, Cl, S, and Mg in concrete were measured according to JSCE-G 574. EPMA was operated at accelerating voltage of 15 kV and probe current of 10 nA, with a probe diameter of 50 $\mu$ m.

(d) Vickers hardness test

Vickers hardness test evaluates the hardness of material based on the size of a depression resulting from an applied force. The Vickers hardness was measured according to JIS Z 2244. The measured depth from the concrete surface was 0.4, 0.6, 0.9, 2, 3, 5, 10, and 15 mm. Measurement was performed at 5~20 points for a depth, because the hardness in concrete varied widely.

## RESULTS AND DISCUSSIONS

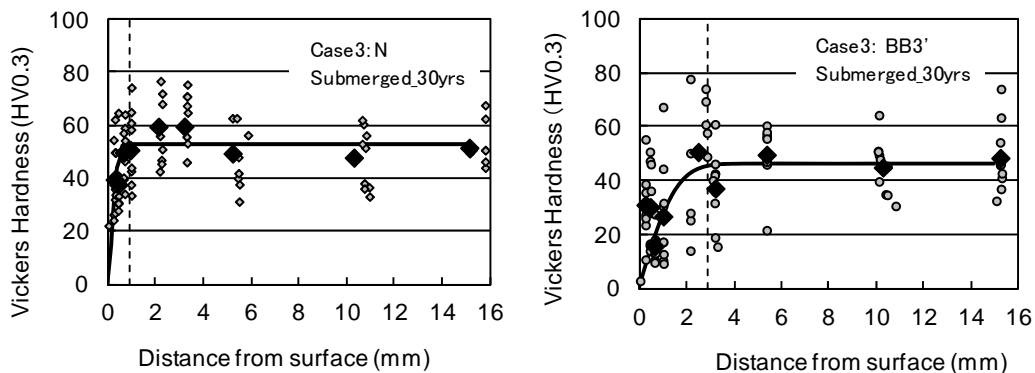
**Compressive strength.** The compressive strength of cores and specimens are shown in Table 2. In most specimens, the compressive strength after exposure increased compared to the initial strength. All cores showed more than 30 N/mm<sup>2</sup>.

**Vickers hardness.** Figure 1 shows examples of Vickers hardness profiles in concrete specimens submerged in seawater for 30 years. Here, a mark ‘◆’ in Figure 1 is showing the average value of 10 points. The average value is low around the concrete surface. On the other hand, the average values inside the concrete were almost constant, and higher than near the surface.

The range where the average value decreased is defined as the ‘deterioration depth’. This depth is shown in Figure 1 as a vertical dotted line. The method to estimate the deterioration depth is shown as below (Yamaji, 2010):

i) The profile of average Vickers hardness is expressed by Eq.(1):

$$H(x, t) = H_0 \cdot erf\left(\frac{x}{2\sqrt{D_H \cdot t}}\right) \quad (1)$$



**Figure 1. Examples of Vickers Hardness Profiles**

(vertical dotted line: deterioration depth)

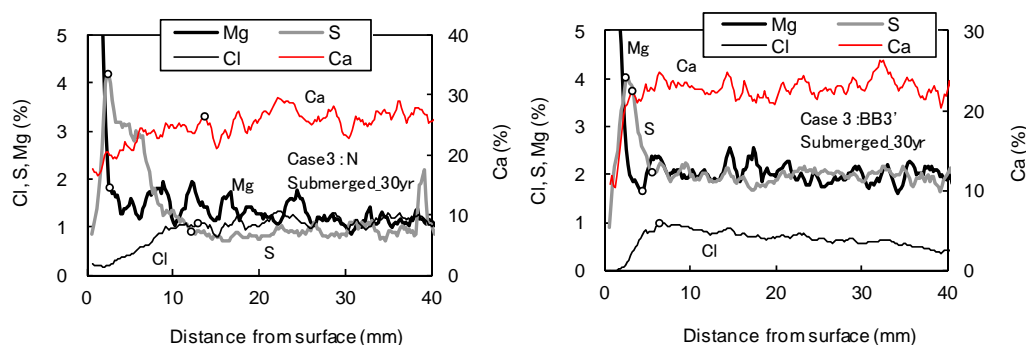
where,  $H(x, t)$  is the Vickers hardness at time:  $t$  (year) and a certain distance from the surface:  $x$ (mm),  $H_0$  is the Vickers hardness of inner concrete (which is assumed to be equal to the initial Vickers hardness value),  $D_H$  is a coefficient which expresses a progress rate of deterioration due to chemical attack ( $\text{mm}^2/\text{year}$ ), and  $\text{erf}(s)$  is an error function.

ii) Eq. (1) expresses the point at which the hardness shows an absolute decrease, as presented by the black line in Figure 1. The point is defined as the deterioration depth, which is the vertical dotted line in Figure 1. The estimated deterioration depth is shown in Table 2. The estimated depth was mostly less than 5 mm.

**Profiles of the concentration of elements in concrete by EPMA.** Figure 2 shows examples of element concentration profiles in paste part of concrete measured by EPMA. The specimens were submerged in seawater for 30 years. The concentration of each element changed around the concrete surface. Some studies have reported the following tendency (Hosokawa, 2007), and the results of this study revealed a similar tendency.

- i) Ca decreased around the surface.
- ii) Cl, S, and Mg penetrated into concrete from the outside. The penetration rate was largest for Cl, next S, and smallest for Mg, in decreasing order.
- iii) Cl decreased in the depth where the concentration of S was high.
- iv) S and Ca decreased in the depth where the concentration of Mg was high.

**Correlation analysis between the deterioration and penetration depths.** The results of Vickers hardness test indicated that the strength of concrete decreased near the surface. Also, in the analysis results using EPMA, the concentration of each element changed near the concrete surface. If the correlation between the deterioration and



**Figure 2. Examples of Element Concentration Profiles by EPMA**

(○: point X in Eq(2))

**Table 4. Standard error ( $S_e$ ) calculated using Eq.(2)**

$Y \backslash X$	Mg	Smax	S	Ca	$y_{cl}$	$y_n$
Deterioration depth	1.2	1.3	8.1	6.0	7.0	2.1
Mg		1.3	7.5	5.4	6.1	1.3

penetration depths of each element is clearly recognized, the penetration depth is considered to be an indicator of concrete deterioration.

Table 4 shows the standard error,  $S_e$ , between  $Y$  and  $X$ , assuming that the regression equation is  $Y = X$ . Here,  $S_e$  is calculated with the equation below:

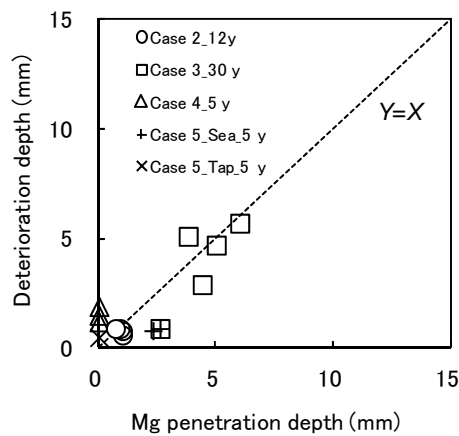
$$S_e = \sqrt{\frac{\sum_{i=1}^n (X - Y)^2}{n - 2}} \quad (2)$$

Here,  $X$  : each factor presented in Table 4 (mm),  $Y$  : deterioration depth (mm),  $n$  : number of data.  $X$  was read using the following methods. An example is shown as a mark 'O' in Figure 2. Each  $X$  is shown in Table 1 and Table 2.

- i) Mg (Mg penetration depth): the point at which the concentration starts increasing.
- ii)  $S_{\max}$ : the point at which the concentration is maximal.
- iii) S: the point at which the concentration starts increasing from the inner to maximum part.
- iv) Ca: the point at which the concentration starts decreasing to the surface.
- v)  $y_{cl}$ : the point at which the concentration starts decreasing to the surface.
- vi)  $y_n$ : the neutralization depth.

$S_e$  was smallest for Mg. Also,  $S_e$  was small for  $S_{\max}$ . This suggested that there was a relationship between concrete deterioration in a marine environment and the penetration of  $Mg^{2+}$  and  $SO_4^{2-}$ . Figure 3 shows the relationship between the deterioration depth and Mg penetration depth, for which  $S_e$  was the smallest, therefore, it can be said that there was a close correlation. This suggested that the Mg penetration depth can be an indicator of concrete deterioration in marine environments.

The reason was considered as following: 1) M-S-H (Magnesium Silicate hydrate), which was produced by the reaction of C-S-H with  $Mg^{2+}$ , was more vulnerable than C-S-H (Santhaman, 2002). 2)  $SO_4^{2-}$  penetration caused the formation of Ettringite in the range of Mg penetration. 3) The Ca concentration was decreased in the range of Mg penetration. Here, the decrease in the Ca concentration is considered to be due to the resolution of  $Ca(OH)_2$  or C-S-H by  $Mg^{2+}$ .



**Figure 3. Relationship between Mg Penetration Depth and Deterioration Depth**

**Trial of the estimation of concrete deterioration in marine environment.** The authors estimated the deterioration of concrete in marine environments using the ‘Mg penetration depth’ as an indicator of deterioration.

Generally, the penetration depth of element in concrete, such as the neutralization depth, is considered to be in proportion to the square root of time:  $t$ . Here, the ‘Mg penetration depth’ is assumed to be also in proportion to the square root of time; as Eq.(3).

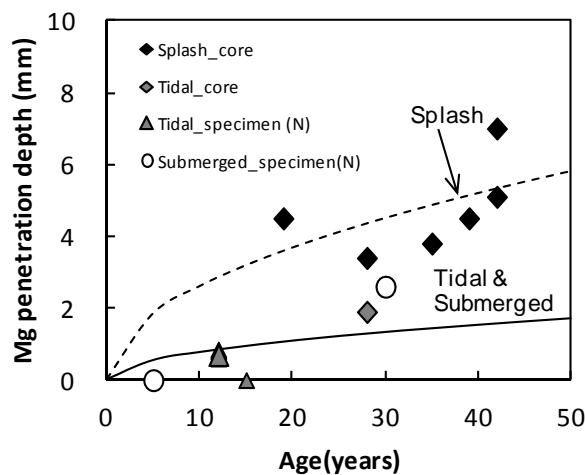
$$y = A t^{1/2} \quad (3)$$

Here,  $y$  is the Mg penetration depth (mm), and  $A$  is a constant ( $\text{mm}/\text{year}^{0.5}$ ). The estimation of deterioration depth is carried out using the ‘Mg penetration depth’ and Eq.(3).

Figure 4 shows the measured and estimated values for the Mg penetration depth. Also, the curve in Figure 4 is estimated using ‘constant:  $A$ ’, which is the average value for each Mg penetration depth.

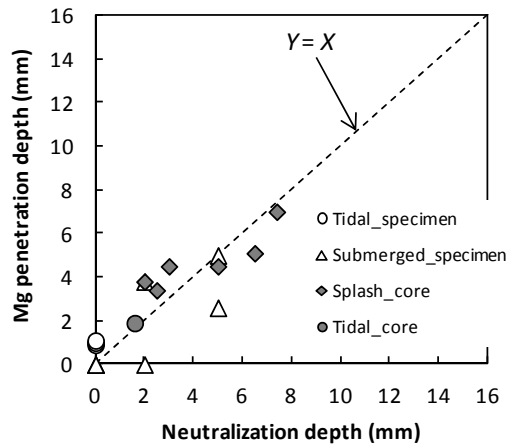
From this estimation result, the progress of deterioration in marine environments is very slow, especially in tidal and submerged environments under wet conditions. On the other hand, the depth under the splash environment became relatively larger compared to that under tidal and submerged environments.

**Correlation with the neutralization depth.** Mg penetrates into cement paste to replace  $\text{Ca}(\text{OH})_2$  at first because  $\text{Mg}(\text{OH})_2$  has lower solubility than  $\text{Ca}(\text{OH})_2$ . After the replacement of  $\text{Ca}(\text{OH})_2$ , Mg replaces Ca in C-S-H to form M-S-H having lower strength. Because of the low solubility of M-S-H, pH is expected to decrease significantly to the level that phenolphthalein does not show purple colour. Figure 5 shows the relationship between the neutralization depth and Mg penetration depth. There is a close correlation. This means that the neutralization depth is also considered to be an indicator of deterioration in a marine environment. If the relationship is always recognized, we can estimate the deterioration of



**Figure 4. Change in Mg Penetration depth with Age**





**Figure 5. Relationship between Neutralization Depth and Mg Penetration Depth**

concrete in a marine environment using the ‘neutralization depth’ as a simple indicator.

## SUMMARY

In this study, in order to investigate the deterioration of concrete in marine environments, both concrete cores sampled from existing structures and test specimens exposed in an outdoor pool of natural seawater were used. Then, these specimens were examined based on the Vickers hardness test, neutralization depth measurements, and measurement of the distributions of various elements by EPMA (Electron Probe Micro Analyzer).

Correlation analysis regarding the distributions of various elements was carried out, and the following important behaviors were observed:

- 1) The penetration depth of  $Mg^{2+}$  was correlated with both the neutralization depth and depth of  $SO_4^{2-}$  penetration.
- 2) Deteriorated area in concrete specimens determined by the Vickers hardness was correlated with the penetration depth of  $Mg^{2+}$ . One of the reasons for this deterioration is considered to be the phase change of C-S-H (Calcium silicate hydrate) to M-S-H (Magnesium silicate hydrate), which has a lower strength than C-S-H.
- 3) This means that the penetration depth of  $Mg^{2+}$  can be an indicator of concrete deterioration in marine environments.
- 4) Also, the neutralization depth can be a simple indicator of concrete deterioration in marine environments, because the neutralization depth was correlated with the penetration depth of  $Mg^{2+}$ .

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