- Technical Paper -

DETERIORATION OF CONCRETES CONTAINING SHIRASU NATURAL POZZOLAN AND LIMESTONE POWDER EXPOSED TO AGGRESSIVE CHEMICAL ENVIRONMENT

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ABSTRACT

This study investigated the deterioration of concretes caused by the attack of an aggressive chemical solution composed of 3% sulfuric acid and 5% magnesium chloride. A part of fine aggregate was replaced with Shirasu natural pozzolan and/or limestone powder. The results showed that after 12 weeks of immersion, the compressive strength loss, neutralization depth and chloride penetration depth of concrete containing Shirasu were lower than those of concrete without Shirasu. The addition of limestone powder can result in more severe deterioration of concrete.

Keywords: Shirasu, limestone powder, sulfuric acid, magnesium chloride, compressive strength, deterioration of concrete

1. INTRODUCTION

Recently, concrete structure has been increasingly subjected to aggressive environment such as presence of sulfuric acid in sewage system, or magnesium chloride deicing salt. Several literatures reported that sulfuric acid solutions dissolve portlandite and decalcify other cement hydration products, resulting in change in microstructural, chemical and physical concrete structure [1,2,3]. In addition, formations of gypsum and ettringite due to chemical reactions cause volume expansion, leading to crack and spalling in concrete structure. Furthermore, Y. Farnam et al. [4] demonstrated that concrete exposed to magnesium chloride solution changes in microstructure due to decalcification of cement hydration products, including formation of brucite, Friedel's salt, magnesium silicate hydrate and secondary calcium oxychloride, leading to significant strength loss of concrete.

In order to improve the performance of concrete against such kinds of aggressive environments, the incorporation of supplementary cementitious material is considered as one of the most common methods. Consequently, many studies on the mineral addition of fly ash, ground granulated blast-furnace slag, silica fume, natural pozzolan or limestone powder to ordinary Portland cement (OPC) have been conducted [2, 3, 6-9].

At present, the addition of limestone to concrete, including as a constituent of cement and as aggregate is common all over the world because of technical and economical advantages, namely workability improvement, the increase in density and impermeability of concrete. The European standard EN 197-1 [5] introduces two types of Portland cement incorporating limestone content up to 20% (type II/ A-L) and up to 35% (type II/B-L). Furthermore, H. Siad et al. [6] showed that the incorporation of limestone powder with glass powder improved sulfuric acid resistance of blended cement mortars. M. Garci et al. [7] reported that the addition of natural pozzolan also displayed the improvement of resistance to sulfuric acid, hydrochloric acid, and sulfate and chloride ions penetration. In addition, in Kyushu island of Japan, the resource of Shirasu natural pozzolan also has exhibited a potential use as building material because of its advantage properties [8].

Deterioration of concrete structures exposed to aggressive chemical environment caused by a variety of natural sources and industrial chemicals is a principal durability concern for service life and maintenance cost of concrete struture. Among aggressive chemical solutions, H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions are considered as the most destructive ions for concrete structures. However, very limited studies have been conducted on deterioration of concrete caused by attack of these ions. Thus, the deterioration of concrete caused by the mixed solution containing sulfuric acid and magnesium chloride as well as effects of Shirasu natural pozzolan and limestone powder as fine aggregate replacement on the resistance of concrete to mixed solution was investigated in this study.

2. EXPERIMENTS

2.1. Materials

The experimental study was carried out on concrete partially replaced with limestone powder (L) and Shirasu natural pozzolan (NP) as fine aggregate. The cementitious

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material used in this study was ordinary Portland cement (C) with a density of 3.16 g/cm^3 and a fineness of 3290 cm^2/g. The chemical compositions of cement, limestone powder and Shirasu natural pozzolan are presented in Table 1. Crushed quartz porphyry was used as conventional fine and coarse aggregates. The density of limestone powder was 2.71 g/cm^3. In addition, the densities of fine aggregate, coarse aggregate, and Shirasu in saturated surface-dry conditions were 2.61, 2.61 and 2.11 g/cm^3, respectively. The water absorption of the fine aggregate, the coarse aggregate and Shirasu were 1.04%, 0.6% and 9.27%, respectively. Regarding the pozzolanic reactivity of Shirasu, it is confirmed that its API (assessed pozzolanic-activity index) value is 14.4 % by using API method [9] which means that it possesses pozzolanic reactivity and is lower than that of commercial low-calcium fly ash with API value of 25~85%.

2.2. Mixture proportion

Mixture proportions of concretes and properties of fresh concretes were shown in Tables 2 and 3, respectively. The concrete mixes had a cement content of 425 kg/m^3, coarse aggregate content of 1005 kg/m^3 and water to cement ratio of 0.40. The replacement ratios of fine aggregate by limestone powder and Shirasu were 5% and 55% by volume, respectively. Mixtures with labels of L5, NP55 and L5NP55 were concretes using limestone powder, Shirasu and both of limestone powder and Shirasu, respectively. Reference concrete (Ref) is defined as concrete with 0% as fine aggregate replacement with limestone powder or Shirasu.

2.3. Specimen preparation and immersion test condition.

Two types of specimen configurations were produced: one was cylindrical specimens of 100 mm in diameter and 200 mm in height and the other was cubic specimens of 100x100x100 mm in size. All of the specimens were cured under seal condition by aluminum adhesive tape at 20°C until the designated test ages.

After 56-day curing at 20^{0}C under seal condition, the specimens were immersed in a mixed solution composed of 3% sulfuric acid and 5% magnesium chloride. Before the immersion, all the surfaces except for an exposure surface of the cubic specimens were coated with acid resistant epoxy resin. For the cylinder specimen for compressive strength measurement after the immersion, top and bottom ends were also covered with the acid resistant epoxy resin. The mixed solutions were refreshed every four weeks.

Besides, companion specimens cured in water were also prepared for reference.

2.4. Measurement items and methods

(1) Portlandite content

The portlandite $Ca(OH)_2$ content was determined by thermogravimetric differential thermal analysis (TG-DTA). The sample was collected from the center part of concrete after the compressive strength test. The aggregate and cement contents in the sample were also determined by the chemical test based on Kansai et al. [10] report as follows. Approximately 0.5 g of powder blends was poured into 200 mL of 15% sodium gluconate solution that has no effect on $CaCO_3$ but can dissolve only cement. Thereafter, the solution was stirred for approximately 30 min by using a magnetic stirrer. Finally, the blends were heated up to 105°C for 12 hours to obtain dried residue. The cement paste content was then calculated directly based on the mass loss of the samples before and after the chemical test. The $Ca(OH)_2$ content was calculated by combining the results of the chemical test and TG-DTA by following formula:

$$CH = \frac{CH_1}{C} \times 100 \quad (2)$$

where,

CH: the amount of $Ca(OH)_2$ as a percentage in cement paste (mass%)

CH_1: the amount of $Ca(OH)_2$ in a sample calculated from the TG-DTA result.

C: the cement paste content in a sample calculated from the chemical test result [10] as follows:

$$C(\%) = \frac{m_s - m_r}{m_s} \times 100 \quad (3)$$

where,

m_s: the mass of the concrete powder sample

m_r: the mass of residue.

(2) X-ray diffraction (XRD) analysis

The main crystalline phase changes in the surface of concrete immersed in the mixed solution and water were identified by using X-ray diffraction analysis. Scanning

Table1. Chemical composition of cement, limestone powder and Shirasu.

Composition %	Cement (C)	Limestone powder (L)	Shirasu (NP)
SiO_2	20.29	0.189	73.61
Al_2O_3	4.91	-	14.69
Fe_2O_3	2.96	0.057	2.63
CaO	65.05	55.75	2.02
MgO	1.20	-	0.28
SO_3	1.93	0.20	0.066
K_2O	0.39	-	3.88
Na_2O	0.26	-	2.27
Cl^-	0.006	-	0.061
LOI	2.44	43.91	2.39

Table2. Mixture proportions of concretes

Mixture	Unit content (kg/m^3)					
	C	W	Fine aggregate			Coarse aggregate
			L	NP	Sand	
Ref	425	170	0	0	758	1005
L5	425	170	39	0	720	1005
NP55	425	170	0	337	341	1005
L5NP55	425	170	39	337	303	1005

Table3. Properties of fresh concrete

Mixture	Slump (cm)		Air content (%)	
	Design value	Measured value	Design value	Measured value
Ref	10.0±2.0	9.5	2.0±0.5	1.8
L5	10.0±2.0	9.5	2.0±0.5	1.8
NP55	10.0±2.0	9.5	2.0±0.5	2.0
L5NP55	10.0±2.0	9.5	2.0±0.5	1.5

with a 2-theta angle ranging from 5^0 to 65^0 using a Cu Kα X-ray source at a rate of 0.5s per 0.02^0 2-theta was adopted. The testing data were analyzed by using EVA program software.

After 12 weeks of immersion in the mixed solution and water, dried powder samples were extracted from the outermost layer of the surface of concrete for the XRD test.

(3) Erosion depth

The erosion depth of specimens immersed in the mixed solution was measured every two weeks after immersion. After being taken out of solution and blotted with paper towels, the length of specimen was measured by using an electronic caliper of 0.01mm accuracy at six points on the specimen. The erosion depth was calculated as the mean of the measured value of three specimens.

$$\text{Erosion depth (mm)} = H_o - H_t \quad (4)$$

where,

H_o: the original depth of specimen before immersion in the mixed solution (mm).

H_t: the depth of specimen after immersion in the mixed solution (mm).

It is noted that in case of expansion of specimen, E value is negative (-)

The measurement of erosion depth of concrete immersed in the mixed solution was shown in Fig.1(a).

(4) Compressive strength loss

The ASTM C267-01 [11] test method was adopted for testing concrete specimens after immersion in the mixed solution. After 12-week immersion in the mixed solution, the specimens were extracted from the solution and blotted with paper towels. The elapsed time between the removal of the specimens from solutions and the compressive tests was 30 minutes in control room at 20^0C. Three specimens of each mixture were tested for the residual compressive strength, which was calculated using the original cross-sectional area of the specimen measured before immersion. The strength loss was calculated by following formula:

$$\text{Compressive strength loss (\%)} = \frac{C_w - C_t}{C_W} x100 \quad (5)$$

where,

C_t: compressive strength of specimen immersed in the mixed solution at the age of immersion time t (N/mm^2)

C_w: compressive strength of specimen cured in water at the age of immersion time t (N/mm^2).

(5) Neutralization depth

The neutralization depth of each specimen was measured using phenolphthalein indicator. After being taken out of solution and blotted with paper towels, the cubic specimens were split into two parts at the middle height of the specimen. After that phenolphthalein solution was sprayed on freshly broken surface of concrete immediately. The color change at the spayed surface was monitored and their depths of color change were measured by using an electronic caliper of 0.01mm accuracy. Nine positions on the split section were measured and the average values of the neutralization depths were calculated. To obtain actual neutralization depth, the erosion depth in Eq. (4) was taken into account as follows:

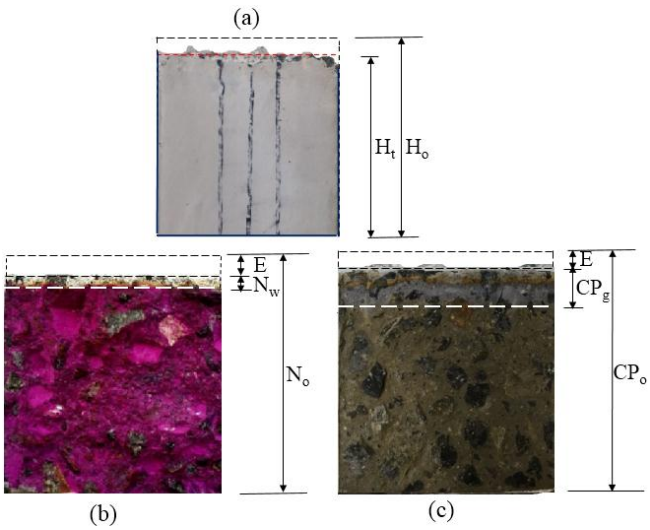


Fig. 1. Erosion depth (a), neutralization depth (b) and chloride penetration depth (c)

$$\text{Neutralization depth (mm)} = N_w + E \quad (6)$$

where,

N_W: the depth of uncolored zone after spraying phenolphthalein solution (mm).

E: erosion depth in Eq. (4) (mm).

The measurement of neutralization depth of concrete immersed in the mixed solution was shown in Fig.1(b). In Fig.1(b), N_o is the original depth of specimen before immersion in the mixed solution.

(6) Chloride penetration depth

The chloride penetration depth of each specimen was measured by spraying silver nitrate indicator. The test procedure of chloride penetration depth measurement is similar to neutralization depth measurement given in the previous section, except for spraying silver nitrate indicator instead of phenolphthalein solution. The actual chloride penetration depth for each concrete was calculated as follows:

$$\text{Chloride penetration depth (mm)} = CP_g + E \quad (7)$$

where,

CP_g: the depth of grey zone after spraying silver nitrate solution (mm).

E: erosion depth in Eq. (4) (mm).

The measurement of chloride penetration depth of concrete immersed in the mixed solution was shown in Fig.1(c). In Fig.1(c), CP_o is the original depth of specimen before immersion in the mixed solution.

3. RESULTS AND DISCUSSION

3.1. Portlandite ($Ca(OH)_2$) content

Fig. 2 shows $Ca(OH)_2$ content of concrete samples at the ages of 3 and 28 days. The results show that at the age of 3 days, $Ca(OH)_2$ contents in the pastes extracted from concretes containing Shirasu (L5NP55 and NP55) were approximately equal to that in the paste of concrete containing limestone powder (L5) and reference concrete (Ref). However, at the age of 28 days, the $Ca(OH)_2$ contents of L5NP55 and NP55 samples were significantly lower than those of Ref and L5. The reduction of $Ca(OH)_2$ content in concrete containing Shirasu after 28-day curing

can be attributed to the consumption of $Ca(OH)_2$ due to pozzolanic reaction [12]. In addition, little difference in the $Ca(OH)_2$ content between L5 and Ref regardless of curing ages demonstrated that the effect of limestone powder on the cement hydration process was insignificant in this study.

3.2. X-ray diffraction analysis on concrete after immersion in the mixed solution.

The XRD pattern shown in Fig.3 confirmed that the peaks of portlandite ($Ca(OH)_2$) dominated in concrete cured in water. However, no portlandite peak was observed in all concrete immersed in the mixed solution due to the attack of sulfuric acid and magnesium chloride. Calcite ($CaCO_3$) in L5 and L5NP55 concrete also absolutely decomposed in L5 and L5NP55 concrete immersed in the mixed solution. In addition, the appearance of large quantity of bassanite ($CaSO_4.0.5H_2O$), gypsum ($CaSO_4.2H_2O$), hydrophilite ($CaCl_2$) and epsomite ($MgSO_4.7\ H_2O$) were confirmed in the XRD patterns of all concrete immersed in the mixed solution. It indicated that the portlandite and calcite was susceptible to aggressive chemical reactions when concrete were immersed in the mixed solution. After immersion in the mixed solution, the hydration products might decompose, followed by the formation of chemical reaction products such as bassanite ($CaSO_4.0.5H_2O$), gypsum ($CaSO_4.2H_2O$), hydrophilite ($CaCl_2$), and epsomite ($MgSO_4.7\ H_2O$).

3.3. Erosion depth

The erosion depths of specimens immersed in the mixed solution is shown in Fig.4. The results show that the expansion process was almost observed until 10 weeks of immersion in the mixed solution for all mixtures. After 12 weeks of immersion, the erosion process was recorded for Ref and L5. On the other hand, the expansion phenomena were still observed in the NP55 and L5NP55 after 12 weeks of immersion in the mixed solution. It is indicated that the addition of Shirasu contributed to slow down the erosion of the concrete immersed in the mixed solution. The occurrence of expansion was attributed to the formation of chemical products of cementitious materials subjected to the mixed solution attack such as gypsum which is usually associated with volume expansion of concrete [1-3]. Over the time of immersion, the cementitious materials and reaction products were dissolved by aggressive chemical attack of the mixed solution, leading to the erosion.

3.4. Compressive strength losses of concrete after immersion

The compressive strength of concrete immersed in the mixed solution and that of concrete immersed in water for 12 weeks is described in Table 4 and the compressive strength loss of concrete after immersion in the mixed solution are illustrated in Fig.5. It can be seen that the highest compressive strength loss of 29.7 % was registered for the concrete mixture containing limestone powder L5. On the contrary, the concrete mixtures containing Shirasu NP55 and L5NP55 showed the lowest compressive strength loss of 22.8% and 23.9%, respectively. It is clearly seen that the addition of Shirasu can improve the resistance of concrete to the aggressive chemical attack of mixed solution composed of sulfuric

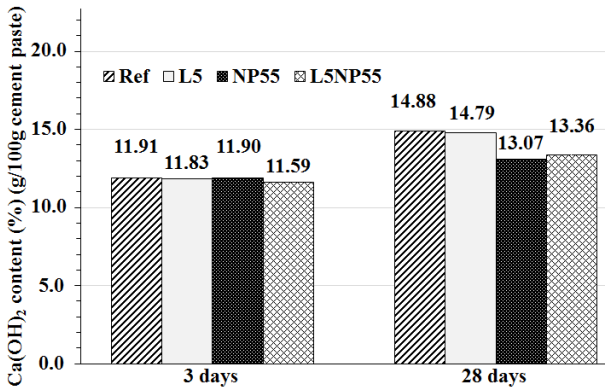
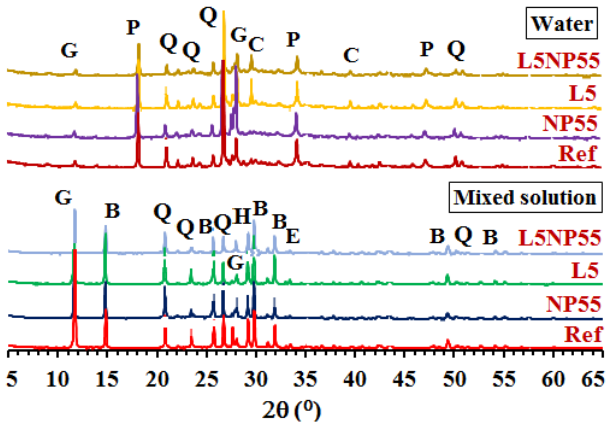


Fig. 2. Content of calcium hydroxide-$Ca(OH)_2$ in pastes of concrete



B: Bassanite ($CaSO_4.0.5H_2O$), C: Calcite ($CaCO_3$), E: Epsomite ($MgSO_4.7\ H_2O$), G: Gypsum ($CaSO_4.2H_2O$), P: Portlandite ($Ca(OH)_2$), Q: Quartz (SiO_2), H: Hydrophilite ($CaCl_2$)

Fig. 3. XRD patterns of concretes after 12 weeks of immersion in water and the mixed solution.

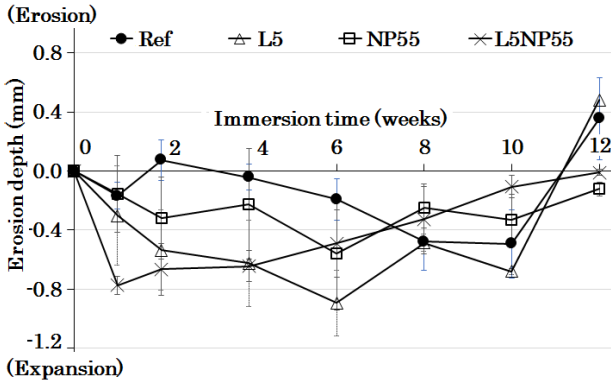


Fig. 4. The erosion depths of concretes after 12 weeks of immersion in the mixed solution.

acid and magnesium chloride. The reason for the higher resistance of NP55 and L5NP55 to the aggressive chemical solution can be the lower Ca(OH)2 content, the result of which is shown in 3.1. It is known that $Ca(OH)_2$ is most vulnerable to aggressive chemical attack [6,7]. In addition, pozzolanic reaction between Shirasu natural pozzolan and $Ca(OH)_2$ in hydrated cement paste can form further hydration products such as secondary calcium silicate hydrates (C-S-H) and calcium aluminum silicate

hydrates (C-A-S-H), leading to the denser cement matrix as well as the reduction in interconnectivity of pores structure [12]. Presumably, these pore structure refinement effects might contribute to the higher impermeability of concrete containing Shirasu. The higher impermeability of concrete containing Shirasu preliminarily showed in the results of neutralization depth and chloride penetration depth as following discussion. The higher impermeability can contribute to impede the penetration of aggressive ions such as H^+, SO_4^{2-}, Mg^{2+}, Cl^- which can damage the concrete structure and reduce compressive strength. On the other hand, L5 concrete contained high amounts of $Ca(OH)_2$ and $CaCO_3$ that were susceptible to chemical reactions which was confirmed in the XRD analysis, resulting in the highest compressive strength loss.

3.5. Neutralization depth

The neutralization depth of concrete after 12 weeks of immersion is described in Fig. 6. It can be seen that concretes replaced with Shirasu as fine aggregate, including L5NP55 and NP55, exhibited the lower neutralization depth in comparison to the concrete without Shirasu, namely Ref and L5. On the other hand, concrete L5 presented the highest neutralization depth. It is approved that Shirasu can enhance the resistance of concrete to the mixed solution attack due to pozzolanic reactivity of Shirasu associated with the lower portlandite content as shown in the results of measurement of the portlandite content in concrete and the refinement effect of concrete structures due to pozzolanic reaction [12]. In contrast, using limestone powder as fine aggregate replacement adversely affected the resistance of concrete because of high contents of portlandite and calcite which were vulnerable to aggressive chemical reactions.

Based on the results of measured neutralization depths together with the assumption that neutralized area has no contribution to concrete strength, the effect of the neutralization depth on the compressive strength loss is preliminarily examined by quantitative analysis as follows.

The effective diameter of non-neutralized concrete exposed to the mixed solution as shown in Fig. 7 was calculated with the assumption as follows:

$$D_m = D_0 - 2xN \quad (8)$$

where,

D_m: the effective diameter of non-neutralized concrete immersed in the mixed solution (mm).

D_0: the original diameter of specimen before immersion in the mixed solution (mm).

N: the neutralization depth of specimen after immersion in the mixed solution (mm). Consequently, based on the effective diameter, the effective compressive strength of non-neutralized concrete immersed in the mixed solution was determined. The results of the effective compressive strength of non-neutralized concrete immersed in the mixed solution was shown in Fig. 8. As can be seen in Fig.8, the trendline of the effective compressive strength of non-neutralized concrete immersed in the mixed solution was 10% lower than the 1:1 line. It indicated that the increase in neutralization depth resulted in significant reduction in the compressive strength of concrete.

Table 4. Compressive strength of concrete specimens after immersion in water and the mixed solution and standard deviation (S.D)

Mixture	Compressive strength (N/mm^2)			
	water	S.D	mixed solution	S.D
Ref	59.4	2.1	42.8	0.1
L5	62.5	1.1	44.0	1.4
NP55	70.4	0.6	54.3	1.1
L5NP55	68.3	0.4	52.0	3.2

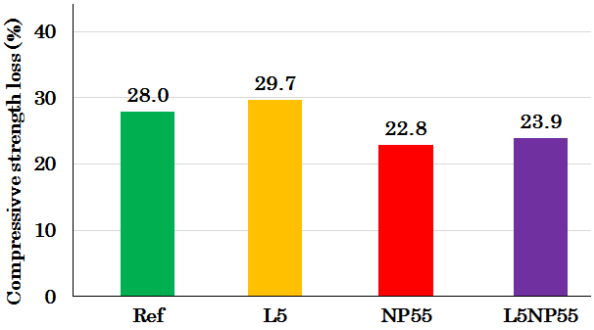


Fig. 5. Compressive strength loss of concrete after 12 weeks of immersion in the mixed solution

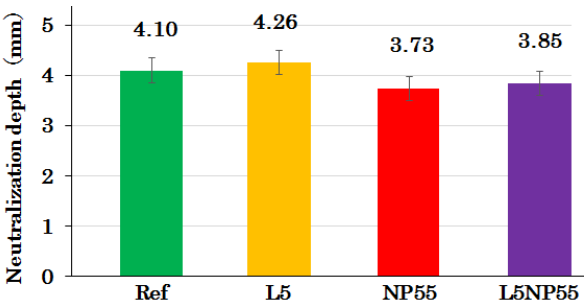


Fig. 6. The neutralization depths of concretes after 12 weeks of immersion in the mixed solution.

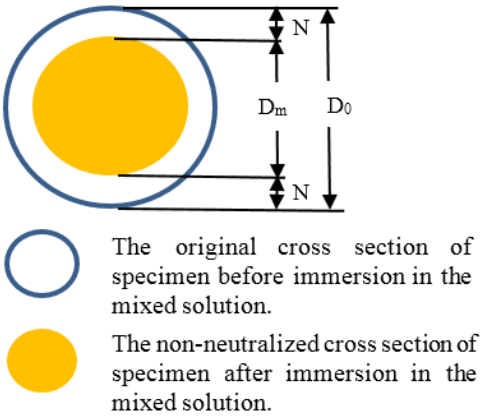


Fig. 7. The change in size of specimen after immersion in the mixed solution.

3.6. Chloride penetration depth

The chloride penetration depth in concrete after 12 weeks of immersion in the mixed solution is presented in Fig. 9. It can be observed that the chloride penetration

depths of L5NP55 and NP55 were lower than those of L5 and Ref. These results indicated that the addition of Shirasu can improve the resistance of chloride ingress. The low chloride penetration of concrete containing Shirasu could be attributed to pore structure refinement effects because pozzolanic reaction resulted in the additional hydration products [12]. The refinement effects might result in the decrease in the connectivity of pores and the densification of concrete structure and contribute to impede the diffusion of ions from external environments into concrete. In addition, using limestone powder also reduced the chloride permeability of concrete, presumably, because the filling effect of limestone powder in the voids between aggregates and cement grains could result in the densification of concrete structure.

4. CONCLUSIONS

This study investigated the deterioration of concrete immersed in the mixed solution composed of 3% sulfuric acid and 5% magnesium chloride and the effect of limestone powder and Shirasu natural pozzolan on the resistance of concrete to the mixed solution attack. Based on this study, the following conclusions can be drawn:

- The deterioration of concrete caused by aggressive chemical containing sulfuric acid and magnesium chloride solution was confirmed by the decomposition of hydration products, calcite of hardened concrete and formation of reaction products, such as gypsum ($CaSO_4.2H_2O$), bassanite ($CaSO_4.0.5H_2O$), epsomite ($MgSO_4.7\ H_2O$), and hydrophilite ($CaCl_2$).
- The utilization of Shirasu as fine aggregate replacement can improve not only the resistance of concrete to aggressive chemical environment but also the chloride impermeability of concrete due to pozzolanic reactivity of Shirasu natural pozzolan.
- The addition of limestone powder as fine aggregate replacement resulted in more severe deterioration of concrete caused by attack of aggressive chemical due to high contents of portlandite and calcite.

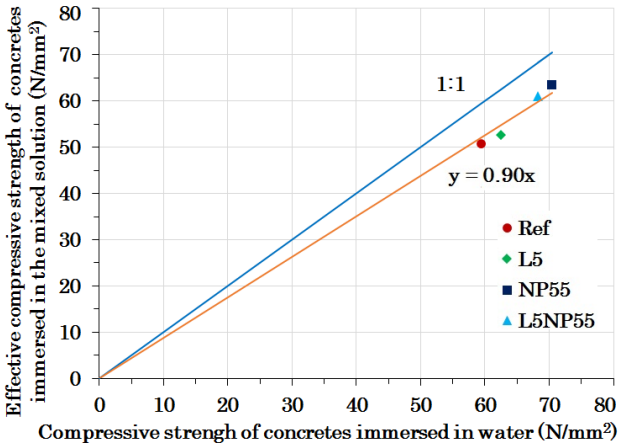


Fig. 8. The reduction of effective compressive strength of concrete immersed in the mixed solution in comparison with that of concrete immersed in water for 12 weeks of immersion.

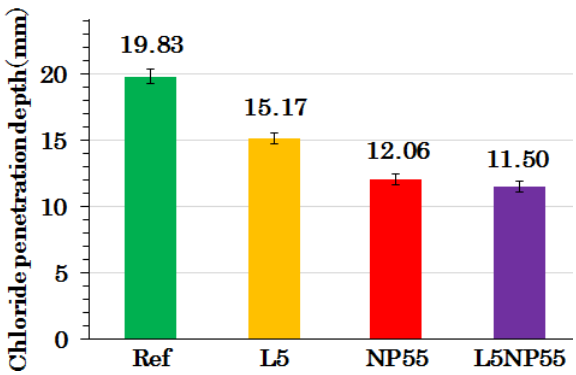


Fig. 9. The chloride penetration depth of concrete after 12 weeks of immersion in the mixed solution

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