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Relation	

EFFECTS OF SHIRASU NATURAL POZZOLAN AND LIMESTONE POWDER ON THE STRENGTH AND AGGRESSIVE CHEMICAL RESISTANCE OF CONCRETE

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ABSTRACT

This study investigated the effects of using limestone powder and Shirasu natural pozzolan, as partial replacements for fine aggregate, on the mechanical properties and resistance of concrete to an aggressive solution containing 3% H_2SO_4 and 5% $MgCl_2$. The data show that replacing 5% of the fine aggregate with limestone powder results in more severe deterioration of the concrete by the chemical solution. However, replacing 55% of the fine aggregate with Shirasu both increases compressive strength after a 28-day cure and improves chemical resistance of concrete. In addition, the deterioration mechanism of concrete immersed in the aggressive solution was examined in this study.

Keywords: Shirasu natural pozzolan, Limestone powder, Sulfuric acid, Magnesium chloride, Compressive strength, Chemical resistance

1. Introduction

Concrete is one of the most widely used building and construction materials, and improvements in the mechanical properties and durability of concrete are always desirable. It has been reported that the replacement of less than 5% of cement by limestone powder accelerates the initial hydration process, increases the amount of hydration products and reduces the porosity of cement-based materials at early ages [1–4]. It has also been established that limestone powder can be combined with manufactured sand to form a fine aggregate capable of filling in pores, accelerating the hydration of the cement and increasing the compressive strength and durability of the concrete [5–7]. The EN 197-1 standard [8] permits the substitution of Portland cement by limestone powder up to a maximum of 35%.

Pozzolan is also commonly used as a supplementary cementitious material in concrete because it provides a number of technical benefits such as enhancement of mechanical properties and durability, as well as an environmental advantage based on reducing the CO_2 emissions of the cement industry. The incorporation of natural pozzolan improves concrete strength because of additional cementitious calcium silicate hydrates [9,10]. Celik et al. [11] also reported that a binary blend of cement with natural pozzolan exhibits higher resistance to chloride migration compared to ordinary Portland cement mixtures. Natural pozzolan has been used not only for cement replacement but also as a substitute for fine aggregates, and in this case improves both the strength and durability of concrete [12]. A large deposit of pyroclastic flows (the so-called Shirasu deposit) covers a wide area of approximately 3500 km^2 in southern Kyushu, Japan. Previous studies [13–16] have established that Shirasu contains a high proportion of amorphous volcanic glass (approximately 60%), which exhibits pozzolanic activity. However, our knowledge of the performance of Shirasu mortar/concrete in terms of mechanical properties and durability remains limited.

Concrete structures must withstand a variety of environmental stresses. Deicing salt, saline, acid sulfate soils and industrial drainage can all degrade the strength of concrete. Many studies have examined the effects of aggressive environments on the durability of concrete [17–23]. The deterioration of concretes subjected to sulfuric acid is characterized by the dissolution of cementitious materials and cracking owing to the formation of gypsum and ettringite, which are associated with the volume expansion of concrete [19–22,24]. Farnam et al. [23] demonstrated that, after immersion in a $MgCl_2$ solution, concrete shows degradation of its microstructure due to the decalcification of cement hydration products and the generation of severe cracks in the concrete.

The incorporation of supplementary cementitious materials is a common means of improving the resistance of concrete to aggressive environments [24–28]. Makhloufi et al. [24] showed that the incorporation of limestone, natural pozzolan, blast furnace slag or silica fume improves the mechanical properties and sulfuric acid resistance of blended cement mortars. The addition of natural pozzolan also improves resistance to sulfuric acid and hydrochloric acid and reduces the penetration of sulfate and chloride ions [12,26,27].

H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions are frequently found in industrial chemical environment, groundwater or acid sulfate soil which affected a huge area worldwide [29]. In addition, the widespread use of $MgCl_2$ as a deicing salt in cold climates is a primary source of deteriorated concrete structures [23,30–32], especially when the salt drains into a sewer system and cooperates with biogenic sulfuric acid in sewer environment [28,33,34]. H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions are considered to be the most destructive ions to concrete and can deteriorate its service life and increase the maintenance cost of civil infrastructures. Therefore, there is an urgent need to study the deterioration mechanism of concrete and identify means of improving the resistance of concrete to aggressive environments. However, only a very few studies have investigated the deterioration of concretes immersed in aggressive chemicals, such as H_2SO_4 and $MgCl_2$ solutions that simulate the aforementioned environments. For the reasons above, the effects of limestone powder and Shirasu natural pozzolan as partial replacements for fine aggregates on the strength and resistance of concretes to an aggressive chemical environment containing H_2SO_4 and $MgCl_2$ were examined in this study.

2. Material and specimen preparation

2.1. Materials

The cementitious material used in this study was ordinary Portland cement (C) with a Blaine fineness of 3290 cm^2/g that conformed to the JIS R 5210 standard (Portland cement) [35]. Limestone powder (L) and Shirasu natural pozzolan (NP) were used as fine aggregates. The densities and chemical compositions of the cement, limestone powder and Shirasu natural pozzolan are presented in Table 1. Crushed quartz porphyry sand and stone were used as conventional fine and coarse aggregates, respectively. The water absorption values of the fine aggregate, coarse aggregate and Shirasu were 1.04%, 0.6% and 9.27%, respectively. The pozzolanic reactivity of the Shirasu was determined using the assessed pozzolanic-activity index (API) method [36] and found to be 14.4% compared to the value for commercial low-calcium fly ash in the range of 25-85%. A water reducing admixture that conformed to the JIS A 6204 standard (Chemical admixture for concrete) [37] was employed to achieve the desired workability for all concrete mixtures.

Table 1. Physical properties and chemical compositions of materials.

Chemical compositions /physical properties	Ordinary Portland cement (C)	Fine aggregate		
		Limestone powder (L)	Natural pozzolan (NP)	Crushed quartz porphyry sand (S)
SiO_2 (%)	20.29	0.19	73.61	75.63
Al_2O_3 (%)	4.91	-	14.69	13.18

Fe_2O_3 (%)	2.96	0.06	2.63	2.08
CaO (%)	65.05	55.75	2.02	1.07
MgO (%)	1.20	-	0.28	0.92
SO_3 (%)	1.93	0.20	0.07	-
K_2O (%)	0.39	-	3.88	5.04
Na_2O (%)	0.26	-	2.27	1.54
Cl (%)	0.006	-	0.06	-
LOI (%)	2.44	43.91	2.39	0.60
Density (g/cm^3)	3.16	2.71	2.11	2.61
Fineness modulus	-	0.08	1.54	2.71

-: Not measured

2.2. Mixture proportions

A constant water/cement ratio of 0.40 and a unit water content of 170 kg/m^3 were used for all concrete mixtures. The proportions of fine aggregate replaced with the limestone powder and Shirasu were 5% and 55% by volume, respectively. The mixture proportions and the fresh properties of the concretes are summarized in Table 2. A reference concrete specimen (Ref) was made without replacing the fine aggregate. Herein, L5 and NP55 designate concretes in which 5% and 55% of the fine aggregate are replaced with limestone powder and Shirasu, respectively, while the L5NP55 is defined as the concrete with both 5% limestone powder and 55% Shirasu as fine aggregate replacements. In this study, limestone powder was used as a partial fine aggregate replacement due to its advantages based on filler, nucleation or chemical effects, and to mitigate disadvantages for the case of cement replacement, such as the dilution effect [38]. The fine aggregate replacement proportion of 5% with limestone powder was based on previous studies [5–7]. The compressive strength and durability of concrete have been found to be enhanced when the mass percentage of limestone powder in the manufactured sand is less than 10-15% [5,6]. The replacement of 55% of the fine aggregate with the Shirasu natural pozzolan was based on the results of a previous study that used an Algerian natural pozzolan as a partial fine aggregate replacement in concrete [12]. Kaid et al. [12] reported that concrete using natural pozzolan as 20% of binder in addition to

13% of fine aggregate exhibited improved compressive strength after 28 days of cure and resistance to an ammonium acid solution (480 g/L).

The particle size distributions of the fine aggregates in each mixture are presented in Fig. 1. These data indicate that the aggregate mixtures containing Shirasu (NP55 and L5NP55) had greater proportions of fine particles with sizes of less than 0.3 mm compared to the formulation recommended by the JIS A 5005 standard (Crushed stone and manufactured sand for concrete) [39]. All fresh concrete mixtures in this study were designed to have a slump of 10.0±2.0 cm and an air content of 2.0±0.5%.

Table 2. Mixture proportions and fresh properties of the concrete specimens.

Mixture	W/C	Unit content (kg/m^3)						Slump (cm)		Air content (%)	
		C	W	Fine aggregate			Crushed quartz porphyry stone	Design value	Measured value	Design value	Measured value
				L	NP	S					
Ref	0.40	425	170	0	0	758	1005	10.0±2.0	9.5	2.0±0.5	1.8
L5	0.40	425	170	39	0	720	1005	10.0±2.0	9.5	2.0±0.5	1.8
NP55	0.40	425	170	0	337	341	1005	10.0±2.0	9.5	2.0±0.5	2.0
L5NP55	0.40	425	170	39	337	303	1005	10.0±2.0	9.5	2.0±0.5	1.5

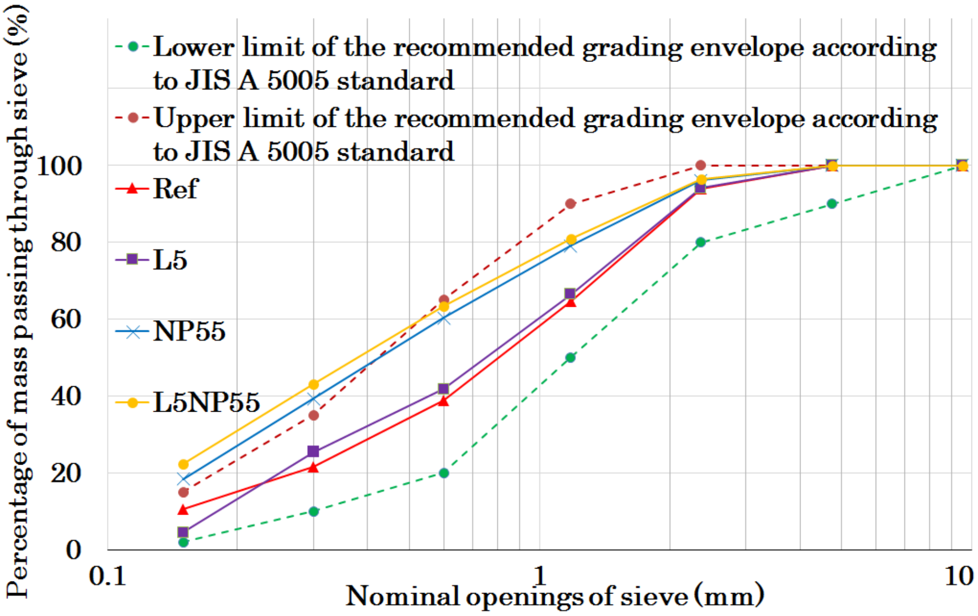

Fig. 1. Particle size distributions of the fine aggregate mixtures.

2.3. Specimen preparation

Two types of specimens were produced: cylindrical specimens with 100 mm diameters and 200 mm heights for compressive strength measurement and cubic specimens with dimensions of 100 × 100 × 100 mm for the other measurements. After casting, specimens of each concrete mixture were cured at 20 °C while sealed with aluminum adhesive tape until tested to prevent water loss and carbonation [40–43].

3. Test procedures and measurements

3.1. $Ca(OH)_2$ content

At ages of 3, 28 and 91 days, the $Ca(OH)_2$ content in the cement pastes of the concrete specimens were ascertained by determining the cement content in each sample using a chemical test, combined with data from thermogravimetric and differential thermal analysis (TG-DTA). The samples for this test were obtained from the center part of concrete specimens following compressive strength tests. Each sample was soaked in acetone for 24 h to stop any further chemical reactions, after which the samples were dried in a vacuum desiccator for 24 h and then crushed into fine powders (maximum particle size of 150 μm) using a milling machine. The resulting homogenous powders were separated into two parts for the determination of cement content using a chemical test and the analysis of $Ca(OH)_2$ content based on TG-DTA.

The sodium gluconate dissolution method [44] was adopted for determination of cement content. This test was performed by adding approximately 0.5 g concrete powder to 200 mL of a 15% sodium gluconate solution. The suspension was mixed using a magnetic stirrer at 300 rpm and gently boiled for 30 min. After stirring, the solution was passed through filter paper and the solid thus captured was dried at 105 °C for 12 h to eliminate free water, followed by cooling in a desiccator to ambient temperature for 30 min. Finally, the mass of the residue after drying was determined.

The $Ca(OH)_2$ content was found using TG–DTA, employing a DTG-60H instrument (Shimadzu Corporation). In each analysis, a sample of concrete powder was heated from room temperature to 100 °C at 20 °C/min, maintained at 100 °C for 30 min to remove free water, and then heated to 1000 °C at 20 °C/min. Based on the cement content results and the TG-DTA data, the $Ca(OH)_2$ content in the cement paste of each sample was determined using the equation

$$CH = CH_1 \times 100 / C, \qquad (1)$$

where CH is the $Ca(OH)_2$ content as a percentage of the cement paste (%), CH_1 is the $Ca(OH)_2$ content in the sample as determined by TG-DTA (%) and C is the cement paste content in the sample as calculated from the chemical test data (%). The last term is calculated as

$$C = (m_s - m_r) \times 100 / m_s, \qquad (2)$$

where m_s is the mass of the concrete powder sample (g) and m_r is the mass of the residue after drying (g).

3.2. Compressive strength

At ages of 3, 28 and 91 days, the compressive strength of each specimen was measured according to the JIS A 1108 standard (Method of test for compressive strength of concrete) [45]. Three specimens were used for the compressive strength test at each age. The compression test was conducted at a constant load rate of 1.5 kN/s.

3.3. Immersion test

3.3.1. Procedures

After being cured for 56 days at 20 °C while sealed with aluminum adhesive tape, the concrete specimens were immersed in a mixed solution containing 3% H_2SO_4 and 5% $MgCl_2$. Prior to immersion, all but one designated surface of each cubic specimen was coated with an acid resistant epoxy resin. In the case of the cylindrical specimens, the two surfaces at both ends of the specimen were coated with this resin. The mixed solution was refreshed two weeks after immersion and every four weeks thereafter so as to maintain a pH in the range of 0.3 to 0.7 for a period of 22 weeks, at a temperature of 20±3 °C. The ratio of the volume of the mixed solution to the surface area of the specimen was fixed at approximately 8 mL/cm^2 to maintain constant contact conditions between the specimen and the solution. Several specimens were also immersed in deionized water for comparison purposes.

3.3.2. X-ray diffraction (XRD) analysis

Dried powdered samples were extracted from the outermost layer of the surfaces of concrete specimens immersed in the mixed solution or in deionized water for 22 weeks. These powders were assessed by XRD to identify the primary crystalline phases, using an AXS D_2 Phaser X-ray diffractometer (Bruker Corporation). Patterns were obtained over the 2θ range from 5^o to 65^o using a Cu Kα X-ray source and the data were analyzed using the EVA software program.

3.3.3. Erosion depth

A typical erosion depth measurement is shown in Fig. 2. After the specimen was removed from the mixed solution and blotted with paper towels, the length of the specimen was determined using an electronic caliper with 0.01 mm accuracy at six points on the sample. The erosion depth was then calculated using the equation

$$\text{Erosion depth (mm)} = H_o - H_t, \quad (3)$$

where H_o is the original length of the specimen before immersion (mm) and H_t is the length of the specimen after immersion (mm). Each specimen was tested in triplicate and the mean values are reported. It should be noted that, in the case that the sample expanded, the erosion depth would be negative.

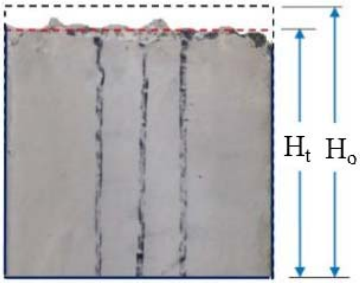

Fig. 2. The measurements of erosion depth

3.3.4. Compressive strength loss

The ASTM C267-01 standard [46] (Test method for chemical resistance of mortars, grouts, and monolithic surfacing and polymer concretes) was used to determine the compressive strength of concrete specimens after immersion in the mixed solution. After 22 weeks of immersion, each specimen was extracted from the solution and blotted with paper towels. The elapsed time between the removal of the specimen from the solution and the compressive strength test was 60 min, at 20 °C. The residual compressive strength of the specimen was subsequently determined, using the original cross-sectional area of the specimen before immersion. For each concrete mixture, three specimens were used for the compressive strength test. The strength loss was determined using the equation

$$\text{Compressive strength loss (\%)} = (C_w - C_m) \times 100 / C_w, \quad (4)$$

where C_m is an average of three test results for specimens immersed in the mixed solution for a period of time, t (N/mm^2) and C_w is an average of three test results for specimens immersed in deionized water for the same period of time (N/mm^2).

3.3.5. Concentration profiles of magnesium, chloride and sulfate ions in concretes

The concentration profiles of Mg^{2+}, Cl^- and SO_4^{2-} ions in the concrete were established by measuring the concentrations of these ions at different depths after 22 weeks of immersion. In preparation for analyses, a powdered sample was collected from the neutralized region of each specimen by abrading the specimen with a handheld mini grinder from the surface to the depth at which the neutralization frontier disappeared (as determined based on the brown coloration between the neutralized and non-neutralized regions; see Fig. 3). In addition, slices were cut from the non-neutralized zone using an oil saw at 5 mm intervals, as shown in Fig. 3. After oil on the surfaces of the slices was blotted with paper towels, the slices were soaked in acetone for 30 min to completely remove residual oil. Then, the mortar samples from slices were collected and dried in a desiccator for 24 h before being ground into powders less than 150 μm in size.

Approximately 1 g of each powder sample was poured into 50 mL of a 2 M HNO_3 solution, after which the solution was covered with a watch glass and stirred magnetically for approximately 30 min at 300 rpm and 100 °C. Subsequently, the suspension was cooled to ambient temperature and filtered, following which the concentration of magnesium ions in the filtrate was determined using a Shimazu AA-6800 atomic absorption spectrophotometer. The concentrations of chloride and sulfate ions were determined using a Dionex ICS-1000 ion chromatography system based on the JIS A1154 standard [47] and a previous report [48].

The concentrations of Mg^{2+}, Cl^- and SO_4^{2-} ions in concrete specimens immersed in deionized water were also ascertained using mortar samples collected from the center part of each specimen.

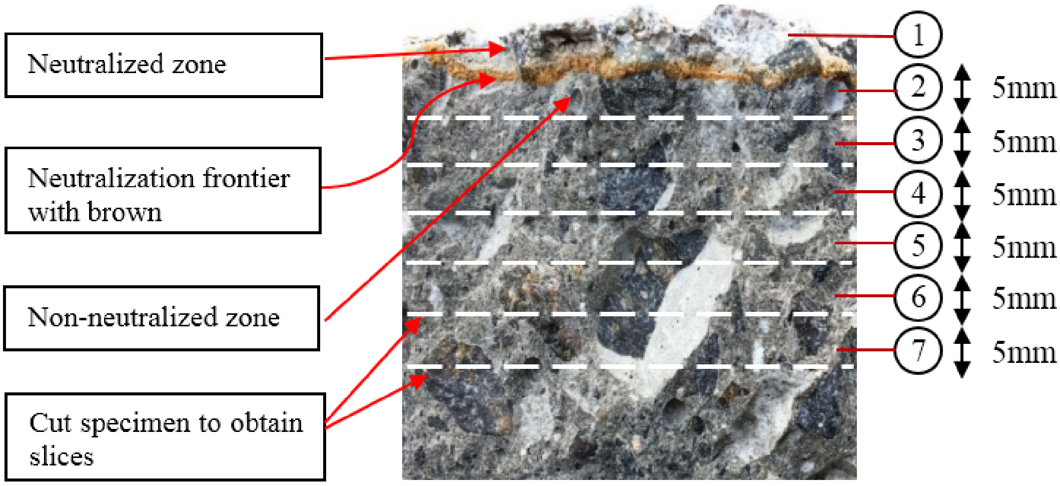

Fig. 3. Sampling of a deteriorated concrete specimen to measure Cl^-, SO_4^{2-} and Mg^{2+} ion concentrations.

4. Results and discussion

4.1. $Ca(OH)_2$ content

Figure 4 summarizes the $Ca(OH)_2$ contents in concrete specimens following aging for 3, 28 and 91 days. It can be seen that, after 3 days, the $Ca(OH)_2$ contents in the pastes extracted from concretes both with Shirasu (L5NP55 and NP55) and without (Ref and L5) were almost equal. However, the $Ca(OH)_2$ contents in the L5NP55 and NP55 specimens were significantly lower than those in the Ref and L5 following 28 and 91 days. These reductions in the $Ca(OH)_2$ content after prolonged aging can be attributed to the pozzolanic reactivity of the Shirasu, which consumes $Ca(OH)_2$ from the cement paste to produce additional cementitious materials such as calcium silicate hydrates (C–S–H) or calcium aluminum silicate hydrates (C–A–S–H) [49]. Thus, pozzolanic reactions evidently proceeded in specimens in which 55% of the fine aggregate was replaced by Shirasu during a 28-day curing under sealed conditions at 20 °C. In addition, the $Ca(OH)_2$ content in the L5 specimen was very similar to that of the Ref specimen regardless of curing time, indicating that the effect of limestone powder on the cement hydration process was insignificant.

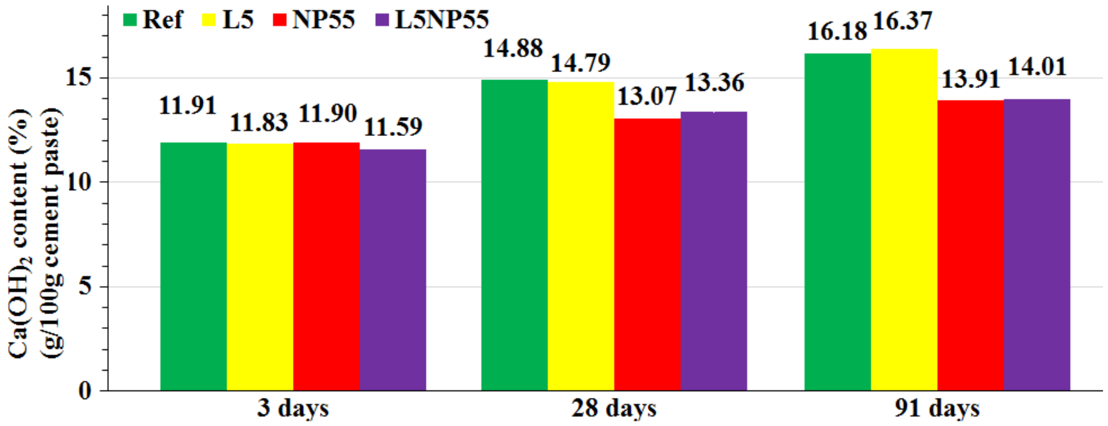

Fig. 4. $Ca(OH)_2$ content in concrete samples at different ages.

4.2. Compressive strength

The compressive strengths of the concrete specimens at different curing ages are presented in Fig. 5. At the age of 3 days, the compressive strengths of the specimens containing Shirasu, including the NP55 and L5NP55, were almost similar to those of the Ref and L5. The effect of adding Shirasu on strength development during this time frame was therefore insignificant under sealed curing conditions at 20 °C. However, at the later ages (i.e. at 28 and 91 days), the compressive strengths of the NP55 and L5NP55 were considerably higher than those of the concretes Ref and L5. Considering the $Ca(OH)_2$ data, it is apparent that the pozzolanic reaction between the Shirasu and $Ca(OH)_2$ produced additional hydration products, resulting in a refinement effect and increased strength after 28 days of curing [9,10,49,50]. The compressive strengths of the NP55 and L5NP55 were almost the same regardless of the aging period. In addition, the compressive strength of the L5 containing limestone powder as a partial fine aggregate replacement was close to that of the Ref specimen after aging for 3, 28 and 91 days. These results indicate that the effect of the limestone powder on the strength development of the concrete was negligible. In contrast, using the Shirasu natural pozzolan as a fine aggregate replacement at a level of 55% improved the compressive strength.

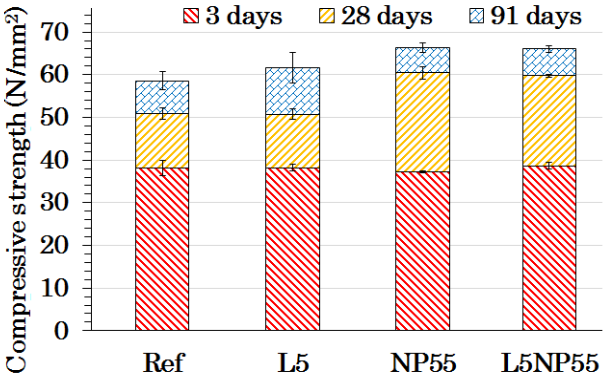

Fig. 5. Compressive strengths of concrete specimens after aging for 3, 28 and 91 days.

4.3. *Immersion test*

4.3.1. XRD analysis

The main crystalline phases of concretes immersed in the mixed solution or in deionized water were identified by XRD. The resulting patterns are provided in Fig. 6. These data indicate that all specimens immersed in deionized water produced similar peaks associated with primary phases of portlandite ($Ca(OH)_2$) or calcite ($CaCO_3$). As an example, the prominent peaks at 2θ values of 18.1°, 34.2° and 47.3° demonstrate the presence of $Ca(OH)_2$. However, there was no trace of $Ca(OH)_2$ in the patterns of concretes immersed in the mixed solution. These results revealed that the $Ca(OH)_2$ was completely decomposed due to chemical reactions with the H_2SO_4 and $MgCl_2$. The intense peaks related to $CaCO_3$ also disappeared in the patterns of those concretes immersed in the mixed solution, indicating that $Ca(OH)_2$ and $CaCO_3$ are vulnerable to chemical reaction with the mixed solution. These results also imply that the presence of $Ca(OH)_2$ as well as $CaCO_3$, a major constituent of limestone powder, resulted in more severe deterioration of the L5 immersed in the mixed solution. The patterns also display prominent peaks related to bassanite ($CaSO_4 \cdot 0.5H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$)

and hydrophilite ($CaCl_2$) in the case of specimens immersed in the mixed solution. The main phases detected by the XRD analysis are summarized in Table 3. These data confirm that the chemical reactions between the mixed solution and cementitious materials such as $Ca(OH)_2$ and C–S–H resulted in a large number of reaction products, including $CaSO_4 \cdot 0.5H_2O$, $CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$ and $CaCl_2$ which are non-cementitious materials. Such reactions led to strength loss and disintegration of the concrete. Reaction products such as gypsum ($CaSO_4 \cdot 2H_2O$) associated with volume expansion can also precipitate and fill in the pores of the concrete, resulting in internal stress and cracking [20–22,51-53].

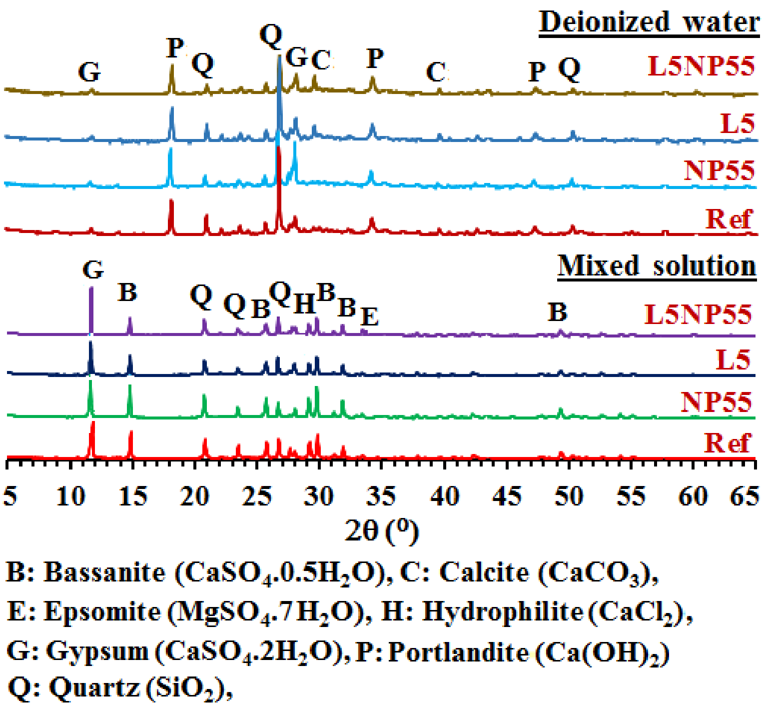

Fig. 6. XRD patterns of concretes immersed in the mixed solution or in deionized water for 22 weeks.

Table 3. Main phases in specimens immersed in deionized water or in the mixed solution as determined by XRD analysis.

Phase	Formula	Peak at 2θ	Remarks
Quartz	SiO_2	20.9°, 26.6°, 50.2°	
Gypsum	$CaSO_4 \cdot 2H_2O$	11.7°, 20.7°, 29.1°	These peaks were more prominent in samples immersed in the mixed solution.
Bassanite	$CaSO_4 \cdot 0.5H_2O$	14.8°, 25.7°, 29.8°, 31.9°, 49.3°	These peaks were only detected in samples immersed in the mixed solution.
Portlandite	$Ca(OH)_2$	18.1, 34.2°, 47.3°	These peaks were more prominent in all samples immersed in deionized water and disappeared in all samples immersed in the mixed solution.
Calcite	$CaCO_3$	29.4°, 39.4°, 43.1°	These peaks were more prominent in the L5 and L5NP55 immersed in deionized water and disappeared in all samples immersed in the mixed solution.
Epsomite	$MgSO_4 \cdot 7\,H_2O$	33.5°	This peak was only detected in all samples immersed in the mixed solution.
Hydrophilite	$CaCl_2$	29.3°	This peak was only detected in all samples immersed in the mixed solution.

4.3.2. Erosion depth

The erosion depths of specimens after immersion in the mixed solution are shown in Fig. 7. Here, a positive value of erosion depth indicates actual erosion of the specimen while a negative value demonstrates expansion. These results show that expansion occurred primarily during the initial 10 weeks of immersion for all specimens. After 12 weeks, the Ref and L5 concretes exhibited significant erosion, while the NP55 and L5NP55 showed slight erosion. After 22 weeks of immersion, the erosion depths of concretes containing Shirasu, including the NP55 and L5NP55, were lower than those of the Ref and L5. These results indicate that the addition of Shirasu slowed the erosion process. The XRD results confirmed the generation of chemical reaction products in all specimens, implying that the observed initial expansion can be attributed to the formation of products such as gypsum or bassanite [20–22,51–53]. However, prolonged immersion resulted in disintegration of the cementitious materials and reaction products due to attack by aggressive chemicals in the mixed solution, leading to dramatic erosion.

The lower erosion depths of the specimens containing the Shirasu (L5NP55 and NP55) may be attributed to the limited $Ca(OH)_2$ contents in the mixtures due to the consumption of $Ca(OH)_2$ through the pozzolanic reactions with the Shirasu. It is known that among the hydration products, $Ca(OH)_2$ is the most likely to react with acids [17,18,54]. Furthermore, the addition of Shirasu may beneficially affect the chemical resistance of the concrete. Prior work has shown that the C–S–H produced by pozzolanic reactions has a denser structure and lower CaO/SiO_2 ratio than conventional C–S–H produced by ordinary Portland cement [20,54]. Chatveera et al. [56] also found that both the chemical composition and CaO/SiO_2 ratio of hydrated cement paste are important factors that determine the resistance to acids. It has also been reported that C–S–H having a high CaO/SiO_2 ratio preferentially undergoes decalcification and is susceptible to further acid attack, while C–S–H with a low CaO/SiO_2 ratio degrades at a slower rate [20,25].

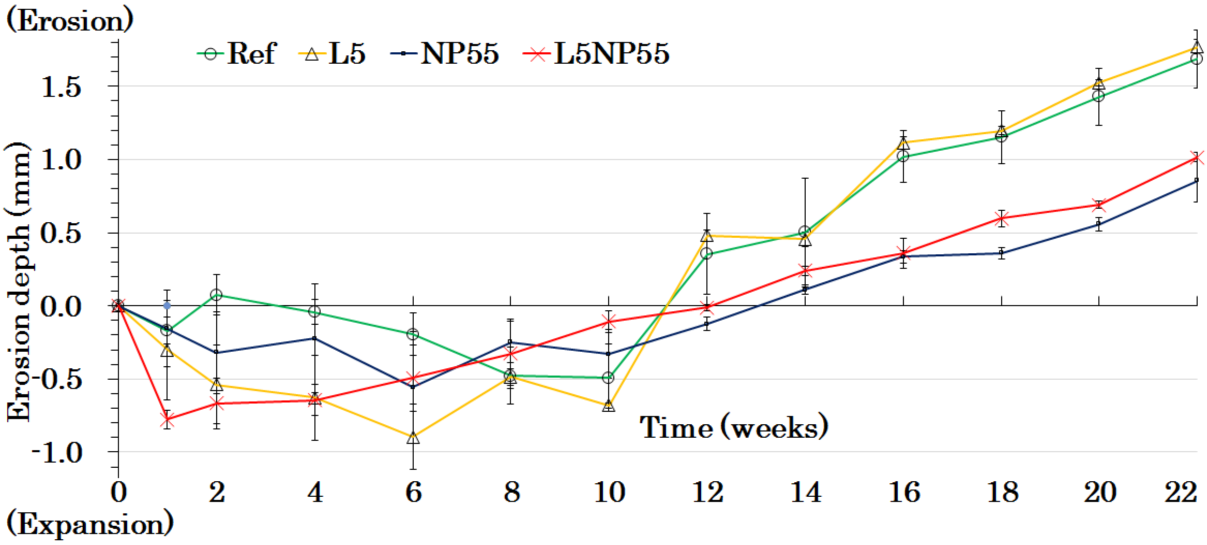

Fig. 7. Erosion depths of concrete specimens during immersion in the mixed solution.

4.3.3. *Compressive strength loss*

The compressive strengths of concrete specimens immersed in the mixed solution or deionized water for a period of 22 weeks are summarized in Table 4. It can be seen that the residual compressive strengths of the specimens containing the Shirasu (NP55 and L5NP55) were significantly higher than those of concretes without the Shirasu (Ref and L5). In addition, in the case of immersion in deionized water, the compressive strengths of the former concretes were higher than those of the latter concretes because of the pozzolanic reactivity of Shirasu (as discussed in Section 4.2).

Table 4. Compressive strengths of concrete specimens after 22 weeks of immersion in deionized water or the mixed solution along with standard deviations (S.D.).

Mixture	Compressive strength (N/mm^2)			
	Deionized water	S.D.	Mixed solution	S.D.
Ref	64.0	1.2	38.2	1.3
L5	64.5	2.5	37.7	3.6
NP55	70.5	1.5	46.1	2.8
L5NP55	68.0	0.4	43.6	0.6

Figure 8 shows the compressive strength losses of the concretes after 22 weeks of immersion in the mixed solution, as calculated using Equation (4). These data indicate that the highest compressive strength loss of 41.6% was associated with the L5. In contrast, the best resistance to the aggressive chemical solution was found in the case of the NP55, with a compressive strength loss of just 34.5%. The $Ca(OH)_2$ content of concretes had a major effect on the deterioration rate, which is associated with the residual strength [17,18,54]. Thus, the lower deterioration rates of the NP55 and L5NP55 can be attributed to the reduced $Ca(OH)_2$ contents in concrete containing Shirasu due to the pozzolanic reactivity of the Shirasu, as seen in Fig. 4. In addition, the pozzolanic reactions of the Shirasu resulted in the formation of additional C–S–H and C–A–S–H, leading to refinement of the pore structure [9,10,49,50]. This microstructure refinement effect prevented the diffusion of H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions into the concrete, leading to reduced deterioration of the concretes. The lower compressive strength losses of the NP55 and L5NP55 are also due to changes in the chemical composition of the hydrated cement paste resulting from the formation of secondary hydration products after the pozzolanic reactions. The pozzolanic reaction of natural pozzolan generates additional calcium-aluminate hydrates that are more stable in highly acidic environments than calcium silicate hydrates [57,58]. In contrast, the greater compressive strength loss of the L5 compared to the Ref specimen can be attributed to the higher $CaCO_3$ content in the former, since $CaCO_3$ will react with the chemicals in the mixed solution, as was determined from the XRD analysis. The resulting reaction products, such as gypsum, are typically associated with the volume expansion of concretes, which in turn can form micro cracks [20–22,51–53]. This phenomenon leads to deeper diffusion of ions and thus an increased the deterioration rate of concrete.

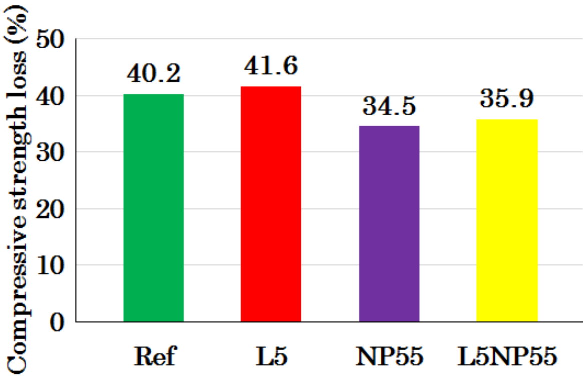

Fig. 8. Compressive strength losses of concrete specimens after 22 weeks of immersion

4.3.4. Concentration profiles of magnesium, chloride and sulfate ions in concretes.

The penetration profiles of Cl^-, SO_4^{2-} and Mg^{2+} ions for the various concretes are presented in Figs. 9, 10 and 11, respectively. According to Fig. 9, the concentration of Cl^- ions decreased with increasing depth from the exposed surface. The chloride penetration depth was approximately 18.5 mm for the specimens containing the Shirasu (NP55 and L5NP55), which is less than the depths of approximately 24.5 mm for the L5 and approximately 29.5 mm for the Ref. These results indicate that using Shirasu as a partial fine aggregate replacement improved the resistance to Cl^- ion penetration. Figures 10 and 11 demonstrate that the concentrations of

SO_4^{2-} and Mg^{2+} ions in concretes immersed in the mixed solution were almost the same as those in concretes immersed in deionized water, except at the shallowest depths. These results suggest that the penetration of SO_4^{2-} and Mg^{2+} ions was essentially stopped at the frontier between the neutralized and non-neutralized zones, as shown in Fig. 3. Thus, the behaviors of these ions differed from that of the Cl^- ions, which passed the neutralization frontier. The deeper penetration of the latter ions is attributed to the more rapid diffusion of Cl^- ions. These results are in agreement with some previous studies [59–62]. Obserholster [59] reported that the diffusion of Cl^- ions is 10-100 times faster than that of SO_4^{2-} ions in concrete, while Stratful [61] determined that the diffusion rate of Cl^- ions was 14 times higher. Bakker [62] reported that the diffusion rate of Cl^- ions in hardened cement pastes is significantly faster than those of SO_4^{2-} and other cations.

In this study, the diffusion coefficients of ions were determined by fitting the ion content plots via a least-squares method using the function

$$C(x,t) = C_o + (C_s - C_o)\cdot\left(1 - erf\left(\frac{x}{2\cdot\sqrt{D_C\cdot t}}\right)\right) \tag{5}$$

where $C(x,t)$ is the ion concentration at depth x and time t (%), C_o is the ion concentration of the concrete prior to immersion (%), C_s is the ion concentration at the surface (%) and D_C is the apparent diffusion coefficient of the ions (m^2/s). The apparent diffusion coefficients (D_C) of the various ions are presented in Table 5.

The results in Table 5 demonstrate that the apparent diffusion coefficients of chloride and sulfate ions in the concretes containing Shirasu, including the NP55 and L5NP55, were lower than those for the concretes without Shirasu (Ref and L5), while the effect of Shirasu on the apparent diffusion coefficient of magnesium ions was not significant. In addition, the effect of limestone powder on the apparent diffusion coefficient of each ion was insignificant. In general, the apparent diffusion coefficient of chloride ions was the highest, and that of magnesium ions was almost equal to that of sulfate ions. In this study, the diffusion coefficient of chloride ions was 6-13 times higher than that of sulfate or magnesium ions.

Table 5. Apparent diffusion coefficients, D_C, of ions after 22 weeks of immersion in the mixed solution.

Mixture	Apparent diffusion coefficient, D_C (m^2/s)		
	Cl^-	SO_4^{2-}	Mg^{2+}
Ref	3.69×10^{-12}	2.80×10^{-13}	3.02×10^{-13}
L5	3.79×10^{-12}	2.83×10^{-13}	2.83×10^{-13}
NP55	1.61×10^{-12}	2.51×10^{-13}	2.89×10^{-13}
L5NP55	2.17×10^{-12}	2.59×10^{-13}	2.96×10^{-13}

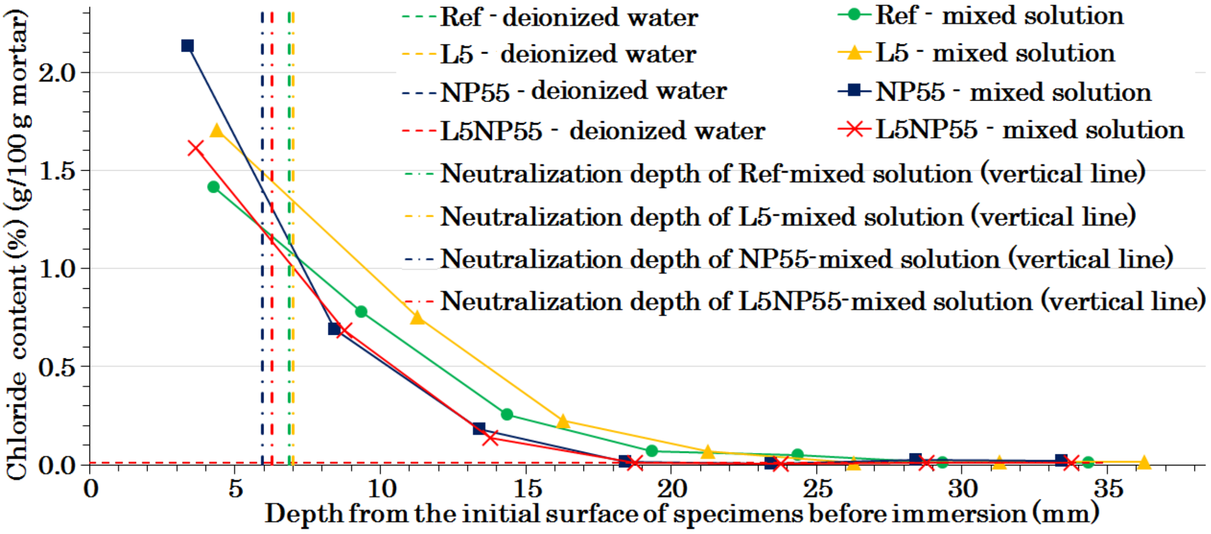

Fig. 9. The Cl^- ion penetration profiles in various concretes after 22 weeks of immersion.

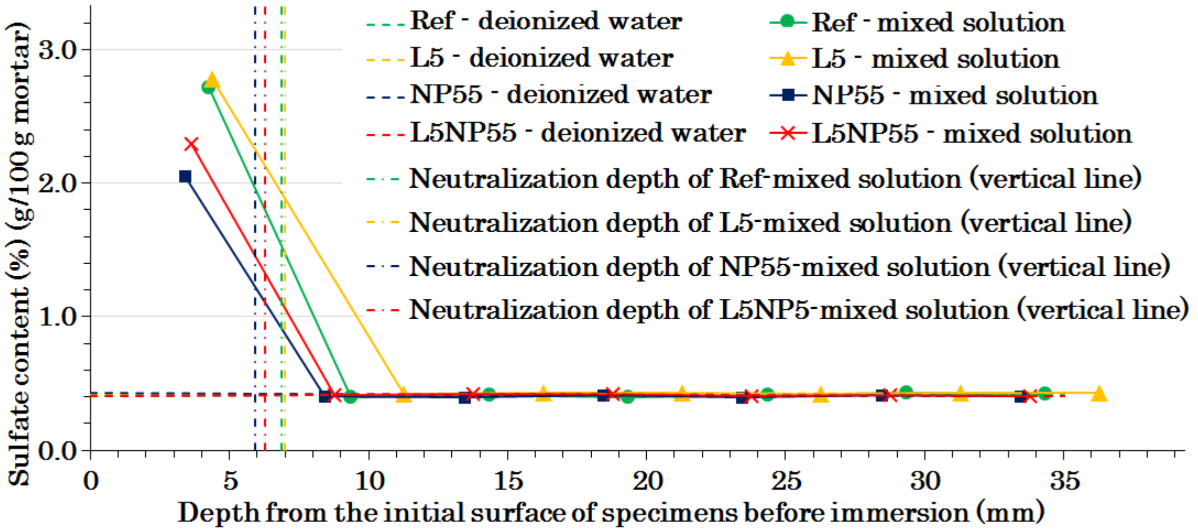

Fig. 10. The SO_4^{2-} ion penetration profiles in various concretes after 22 weeks of immersion.

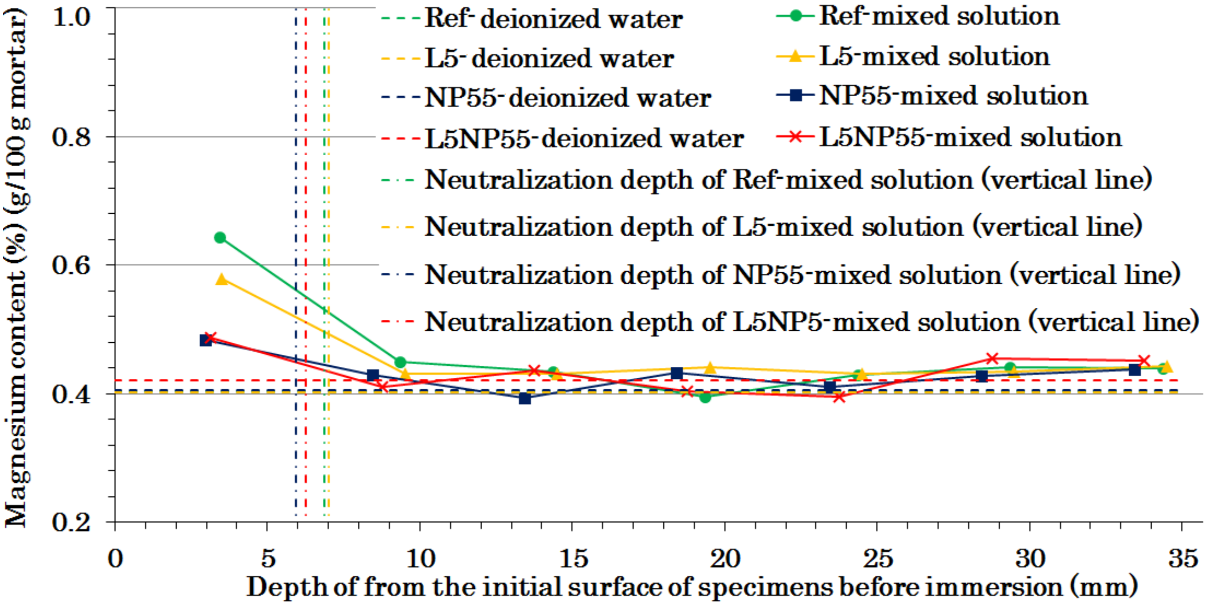

Fig. 11. The Mg^{2+} ion penetration profiles in various concretes after 22 weeks of immersion.

5. Conclusions

This paper presents a detailed study of the strength development and chemical resistance of concretes containing limestone powder and the Shirasu natural pozzolan as fine aggregate replacements. The following conclusions can be drawn based on the mechanical and chemical analyses in this work.

- Concrete containing 55% Shirasu as a fine aggregate replacement exhibited higher compressive strength than concretes without Shirasu after aging for 28 and 91 days under sealed conditions at 20 °C, because of the pozzolanic reactivity of the Shirasu.
- The contribution of limestone powder to strength development was insignificant.
- The use of Shirasu as a fine aggregate replacement improved the resistance of the concrete to an aggressive chemical solution containing 3% H_2SO_4 and 5% $MgCl_2$.
- The addition of limestone powder as a partial fine aggregate replacement resulted in more severe deterioration of concretes by the aggressive chemical solution. However, incorporation of the Shirasu compensated for this effect, such that concrete containing 5% limestone powder

and 55% Shirasu showed higher compressive strength and greater resistance to chemical attack as compared to a reference concrete containing only conventional fine aggregate.

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