Effects of Shirasu Natural Pozzolan and Limestone Powder on the Strength Development and Chemical Resistance of Concrete

（しらすならびに石灰石微粉末がコンクリートの圧縮強度および化学抵抗性に及ぼす影響）

HIROSHIMA UNIVERSITY

March 2020

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ABSTRACT

Concrete is the most widely used construction material and concrete structures have been faced with a variety of aggressive environment. Recently, seawater in coastal acid sulfate soils contains many aggressive chemical compositions for concretes structure and affects huge areas in the world. In addition, the environment in some sewer systems can become very aggressive, especially in the case of sulfuric acid formed by the bacterial action or industrial products combined with magnesium chloride which is used as deicing salt in cold climate areas and drains into the sewer system. In these environments, H^+, SO_4^{2-}, Mg^{2+}, Cl^- ions are considered as the most destructive ions for concrete structures. However, very limited studies have examined the detrimental effect of these ions on the durability of concrete which associated with the service life and maintenance cost of civil infrastructure. The present study aims at investigating the effect of Shirasu, a large deposit of pyroclastic flows in Kyushu island of Japan, and limestone powder as fine aggregate in concrete with respect to compressive strength improvement and the chemical resistance of concrete against aggressive environments containing H^+, SO_4^{2-}, Mg^{2+}, Cl^- ions.

To achieve the above-mentioned purposes, this thesis is divided into of sixes chapters, and detailed organization of the thesis is described as follows:

Chapter 1 presents the background, purposes, and methodology of this study.

Chapter 2 provides a brief literature review on strength development and durability of concrete by considering the effects of limestone powder and Shirasu natural pozzolan.

Chapter 3 presents the experimental program consisting of materials, the mixing, and the casting procedure. In this study, Shirasu and limestone powder were used as a partial fine aggregate replacement. The replacement ratios of fine aggregate by limestone powder and Shirasu were 5% and 55% by volume, respectively, based on referring to some previous studies. After casting, specimens of each concrete mixture, including cylindrical ones with 100 mm

diameters and 200 mm heights and cubic ones with dimensions of 100 × 100 × 100 mm, were separated into two groups: one was stored under normal curing temperature condition in which specimens were cured in a sealed condition with aluminum tape at 20°C until the designated test ages (i.e., 3, 28, and 91 days for the compressive strength test); whereas other was placed under sealed condition with aluminum tape at high curing temperature history of 60°C for 8 hours followed by cooling process in the curing chamber. For the immersion test, specimens cured until the age of 56 days were immersed in a mixed solution containing 3% H_2SO_4 and 5% $MgCl_2$. The effects of limestone powder and Shirasu on properties of concrete cured at different initial temperatures were evaluated via the measurement of compressive strength, $Ca(OH)_2$ content by using thermogravimetric analysis, X-ray diffraction analysis, erosion depth, chloride penetration depth, the mass loss and compressive strength reduction after immersion in the mixed solution.

Chapter 4 discusses the effects of limestone powder and Shirasu natural pozzolan on the strength development and chemical resistance of concretes cured in normal curing temperature with sealed aluminum adhesive tape through microstructural and chemical investigations. The results showed that the use of Shirasu natural pozzolan as a fine aggregate replacement can improve the strength development of concretes after 28 days curing. In addition, after 22 weeks of immersion in the mixed solution, the compressive strength loss, neutralization depth and chloride penetration depth of concretes containing Shirasu were lower than those of concretes without Shirasu. It indicated that the replacement of fine aggregate with Shirasu can improve not only the compressive strength but also the chemical resistance of concrete to the aggressive environment. In contrast, the role of limestone powder in the improvement of compressive strength was insignificant. In addition, after immersion in the mixed solution, highest compressive strength loss, neutralization depth, erosion depth of concretes containing limestone powder was attributed to the higher contents of portlandite and calcite which were vulnerable to the aggressive chemical reaction.

Chapter 5 discusses the effects of different initial curing temperatures on the strength development and chemical resistance of concrete to the mixed solution through microstructural and chemical investigations. The results demonstrated that initial high curing temperature increased the compressive strength of concrete after aging for 3 days but reduced it at later ages (i.e. 28 and 91 days) in comparison with that of concrete cured at normal temperature of 20°C. In addition, initial high curing temperature can accelerate the pozzolanic reactivity of Shirasu, leading to an increase in the compressive strength of concretes containing Shirasu. Furthermore, the deterioration of concretes cured at high temperature by the attack of the mixed solution was less severe than that of concretes cured at normal temperature.

Chapter 6 states the conclusions of this research. Recommendations for future work are also provided.

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Pham Van Toan

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Chapter 1. INTRODUCTION

1.1. General background

Concrete is the dominant construction material used in the infrastructure and superstructure works, therefore the improvements in the mechanical properties and durability of concrete are always desirable. However, production of cement has also caused heavy environment pressure as a result of its global contribution to CO_2 emission. The use of supplementary cementitious materials such as natural pozzolan can improves the workability, mechanical properties and durability of concrete as well as alleviates the environmental burden [1–5]. A large deposit of pyroclastic flows (the so-called Shirasu deposit) covers a wide area of approximately 3500 km2 in southern Kyushu, Japan. Previous studies [6–9] 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.

Limestone is one of possible alternatives due to its wide availability and low cost. It has been reported that filler limestone powder could fill the void of cement particles and improve the packing density of cementitious materials. The incorporation of fine limestone powder can accelerates the initial hydration process, reduces the porosity of cement-based materials and improve the compressive strength concrete at early ages [10–13]. It was also found that limestone powder can be incorporated 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 [14–16].

In addition, the hydration of cement and the pozzolanic reactivity of supplementary cementitious materials such as fly ash or natural pozzolan are significantly affect by temperature [1,17–20]. It is found that the compressive strength of concrete containing supplementary cementitious materials increased remarkably under steam and autoclave curing condition, while the flexural strength compared to those after room temperature curing. High curing temperature also resulted in decrease in porosity and improvement in strength in the interfacial transition zone (ITZ) between cement matrix and aggregate/ fiber [21–23].

In addition, degradation of concrete structure exposed to aggressive environment is a primary durability issue. Regarding the deterioration of concrete in sulfuric acid environment which can occur in concrete structures exposed to ground water, water in acid sulfate soil area [24], chemical waste or especially when deicing salt drains into a sewer system and cooperates with biogenic sulfuric acid in sewer environment [25–29]. Among ions in these environments, 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.

1.2. Objectives of the research.

The goal of this research was to provide a comprehensive understanding of the effects of Shirasu natural pozzolan and limestone powder on the strength development and the chemical resistance of concrete cured under different initial temperature through physicochemical and microstructural investigations. The specific objectives of this research were as follows:

- To study the effects of pozzolanic reactivity of Shirasu natural pozzolan and limestone powder on strength development and chemical resistance of concrete to aggressive chemical environment containing 3% sulfuric acid and 5% magnesium chloride which is produced to simulate the aggressive chemical environment.

- To investigate the effects of curing temperature on the strength and resistance of concrete to attack of the mixed solution.
- To examine the deterioration mechanism of concretes caused by the attack of the mixed solution.

1.3. Methodology of the research

First, to investigate strength development of concrete concerning the effect of limestone powder and Shirasu natural pozzolan on the hydration and pozzolanic processes; four types of concrete mixtures were produced with cylindrical specimen of size 100 mm in diameter and 200 mm in height for compressive strength measurement. The specimens were sealed and cured under different initial curing temperature conditions: one is normal curing temperature at 20 ^{0}C until the designated test ages; other is high curing temperature history of 60°C for 8 hours followed by cooling process. The compression test was performed at the age of 3, 28, and 91 days to examine strength development. The chemical and microstructural tests such as thermogravimetry (TG-DTA) were conducted in order to explain the strength development.

Second, to investigate the effect of limestone powder and Shirasu natural pozzolan on the resistance of concrete to the aggressive chemical environment. The immersion test in a mixed solution containing 3% sulfuric acid and 5% magnesium chloride were carried out after 56 days of cure. After 22 weeks of immersion, the erosion depth, compressive strength loss, neutralization depth, chloride penetration depth measurement were carried out to investigate the resistance of concrete to the aggressive chemical environment.

Finally, after 22 weeks of immersion, XRD analysis and the establishment of concentration profile of ions in the specimens were employed to determine the deterioration mechanism of concrete caused by the attack of the mixed solution,

1.4. Thesis outline

This thesis is divided into of sixes chapters, and detailed organization of the thesis is described as follows:

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Chapter 2 provides a brief literature review on strength development and durability of concrete by considering the effects of limestone powder and Shirasu natural pozzolan.

Chapter 3 presents the experimental program consisting of materials, the mixing, and casting procedure.

Chapter 4 discusses the effects of limestone powder and Shirasu natural pozzolan on the strength development and chemical resistance of concretes to the mixed solution through microstructural and chemical investigations.

Chapter 5 discusses the effects of different initial curing temperature on the strength development and chemical resistance of concrete to the mixed solution through microstructural and chemical investigations.

Chapter 6 states the conclusion of this research. Recommendations for future work are also provided.

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Chapter 2. LITERATURE REVIEWS

2.1. Effect of limestone powder on the properties of concrete

Limestones are sedimentary rocks primarily of calcite, aragonite, vaterite and amorphous calcium carbonate. Limestone powder is crushed and ground from natural limestone or as a by-product of the limestone quarry. Limestone powder has been widely used in concrete due to its availability and low cost. It is reported that limestone powder can influence concrete properties by filler, nucleation, dilution and chemical effects. The action of limestone majorly depends on its fineness and amount [1,2].

2.1.1. Filler effect

The filler effect refines the microstructure, reduces the porosity of cement-based materials. The filler effect of limestone powder majorly relates to its particle size. If the particle size of limestone powder is finer than cement particles, limestone powder will fill the gaps between cement particles and improve the particles size distribution and finally increase the packing density of cement-based materials [3]. Although the incorporation of fine limestone powder can fill the voids between cement particle, the incorporation of limestone powder will reduce the flowability of cement-based materials if its particles size was too small since its specific surface area was high [1]. The flowability of ultrahigh-performance concrete (UHPC) decreased by 27% in the case of 3% nano limestone incorporation [4,5].

2.1.2. Nucleation effect

Nucleation effect accelerates the hydration of C_3S, increases the amount of hydration products and reduces the porosity of cement-based materials at early ages. It is reported that fine limestone powder provides nucleation sites for hydration products to deposit, accelerates the hydration reaction [6,7]. The improved precipitation of C-S-H on the surface of limestone powder was attributed to the similarity between the planar configuration of Ca and O atoms in calcite and CaO layers in C-S-H [8].

The particles size, surface structure and amount of limestone powder affect the nucleation of limestone powder [9–11]. The hydration products of cement tend to envelop the surface of limestone powder particles with similar structures which regard to Ca and O atoms in calcite and CaO layer in C-S-H. With the increase of limestone powder amount, more nucleation sites are available, more hydration products could be absorbed. The surface energy and absorption capacity of limestone powder particles increase as its particle size decreases [1]. As shown in Fig. 2.1, the main hydration peak of the sample containing the finest limestone powder (i.e., median particle size = 0.7μm) was 25% higher than that of the OPC mixture. With the increase of particles size of limestone powder, the heat release curves become close to that of the OPC mixture. It was reported that the nucleation effect of fine limestone powder can promote the precipitation of hydration products and increase the hydration degree of cement, as a result, more hydration heat released [12].

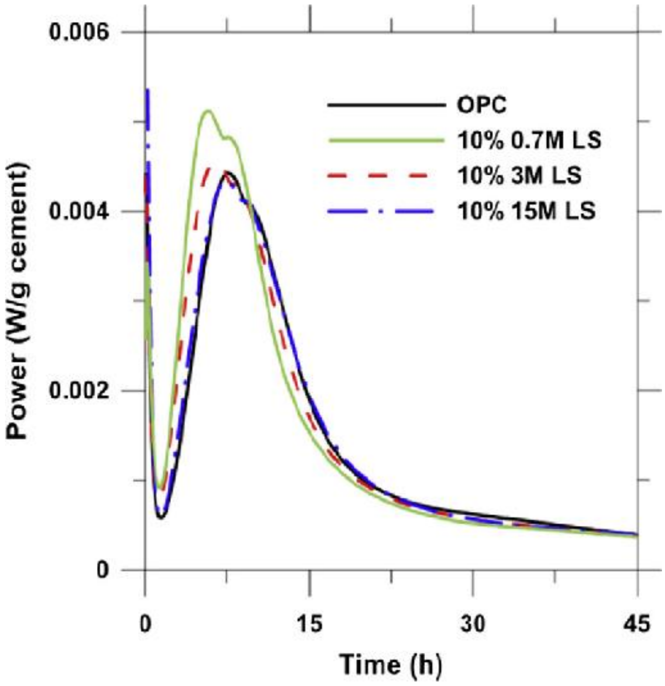


Fig. 2.1. Influence of particles size of limestone powder (LS) on the heat release rate [9].

2.1.3. Dilution effect

The dilution effect reduces the hydration peak of C_3S and the amount of hydration products but increases the porosity of cement-based materials. The dilution effect of limestone powder on the hydration process of cement-based materials is mainly influenced by its amount, especially when the limestone powder with coarse particle size is used. Fig. 2.2 shows that in case of incorporation of coarse limestone powder of 20 µm, the total hydration heat of mixtures containing coarse limestone powder was lower than that of pure Portland cement mixture, and it tended to decrease with the increase of limestone powder amount [11]. It is also found that a higher replacement of cement by limestone powder remarkably reduced the $Ca(OH)_2$ content of cement-based materials [12].

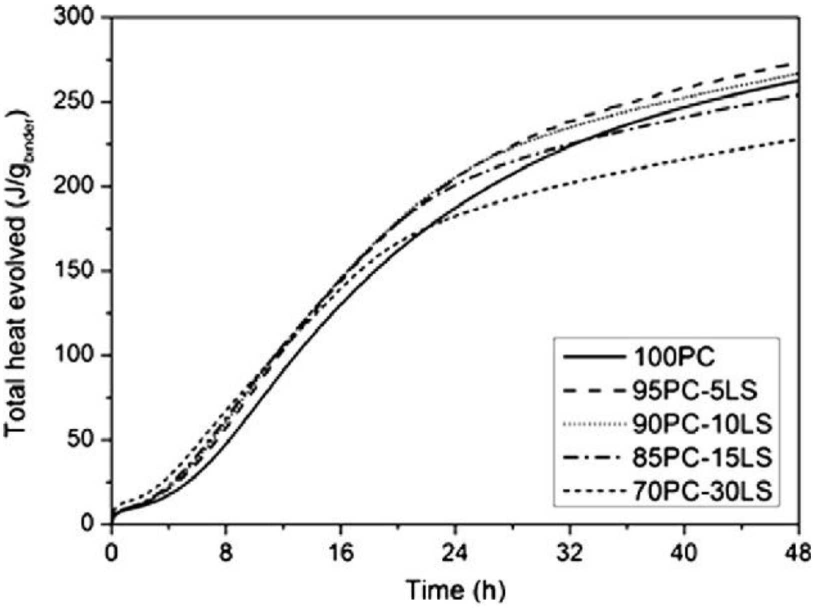


Fig. 2.2. Heat of hydration of Portland cement-20 µm limestone [12]

2.1.4. Chemical effect

The chemical effect promotes the formation of carboaluminate and reduces the porosity of cement-based materials.

The chemical effect of limestone powder on hydration products of cement-based materials is majorly influenced by its particle size and amount and the content of alumina from C_3A and C_4AF in cement as well as its synergic effect with supplementary cementitious materials (SCMs) [1]. With the reduction in limestone powder size, the dissolution of calcium carbonate enhanced and the chemical reaction between calcium carbonate and aluminate increased [9].

The XRD data presented in Fig. 2.3 shows that the aluminate phase reacted with $CaCO_3$ to form mono-and hemi-carbonate when limestone powder was incorporated into cement-based materials [13]. The peak corresponding to hemicarbonate was observed after 7 days. Later, the peak of hemicarbonate decreased but the peak of monocarbonate increased. It is also found that calcium hemicarboaluminate was formed at early ages in the OPC blend containing limestone powder, and it was converted into calcium monocarboaluminate after 28 days [14]. However, it was also reported that the hydration degree of limestone powder was very low at early ages, and the calcium monocarboaluminte hydrates were detected at 180 days [15].

It is also reported that both calcium hydroxide (CH) and carboaluminate content could be influenced by the amount of limestone powder. 5% limestone powder replacement for cement decreased the normalized calcium hydroxide content after 7 days. The decrease in CH content indicated that the formation of calcium hemicarboaluminate hydrate could consume CH [13].

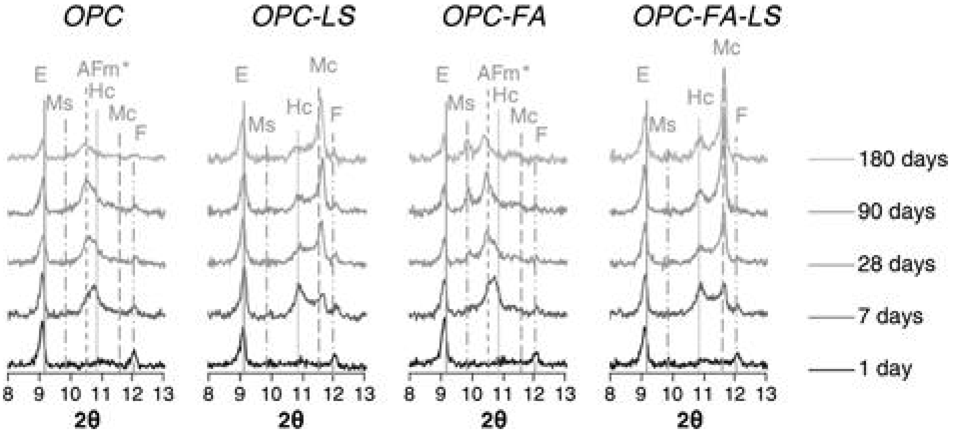


Fig. 2.3. XRD-patterns for the different tested blends at 1, 7, 28, 90 and 180 days. The main peaks of ettringite (E), monosulphate (M_s),possibly a sulphate and carbonate containing hydroxy-AFm(Afm*), hemicarbonate (H_c), monocarbonate (M_c) and ferrite (F) were observed [13].

2.1.5. Effect of limestone powder on fresh concrete

Workability

It is reported that the incorporation of limestone powder improved the workability of concrete [16–18]; while some scholars demonstrated that incorporating limestone powder reduced the flowability of concrete. It is also found that there was an optimum content of limestone powder for the workability of concrete [19]. Effect of limestone powder on the workability of concrete could be mainly attributed to the morphological effect, filler effect and dilution effect. The nucleation and chemical effects occur at several hours of hydration, they seem to have an insignificant effect on the workability of concrete [2].

Incorporation of limestone powder reduces the cement content, and the effective W/C increases. As a result, the electrostatic interaction between cement particles decreases, leading to the higher workability of concrete [20]. It was also reported that incorporating limestone powder reduced the water consumption of concrete [21–23] but the workability of concrete increased as the limestone powder content increased less than 20% [24,25].

Setting time

Effect of limestone powder on the setting time of concrete could mainly be attributed to the nucleation and dilution effects; while the chemical effect occurs after the setting time. When limestone powder particle size is finer than cement particles, limestone powder mainly shows the nucleation effect and dilution effect. When the particle size of limestone powder is equal to or coarser than cement particles, limestone powder mainly shows the dilution effect. Incorporating a small quantity of fine limestone powder acts as the nucleation site and reduces the setting time of concrete. The nucleation effect of limestone powder depends on its particle size and content and the mixture proportions of concrete [2]. Sato et al. [26] demonstrated that the incorporation of nano-limestone significantly accelerated hydration reactions at the early age. Acceleration of the hydration was not observed when coarser limestone powder with a median particle size of about 4 μm [13] or 16 μm [27] was added to replace cement. The replacement of fine aggregate with limestone powder acting as the nucleation sites resulted in a reduction in the setting time of concrete. Due to the nucleation effect of limestone powder, the setting time of concrete increased with the decrease of the limestone powder content, as shown in Fig. 2.4.

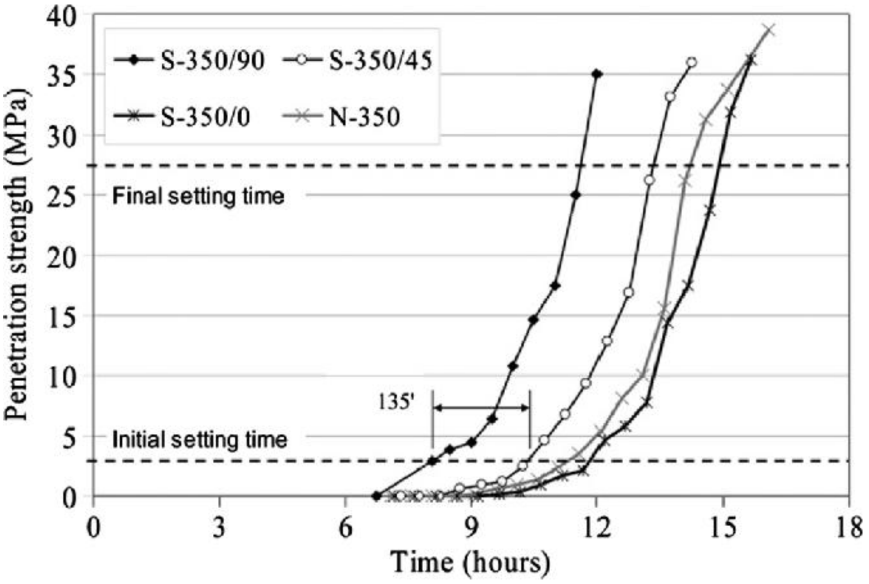


Fig. 2.4. Setting time of concrete with 350kg/m^3 of cement with different limestone powder content [28]

2.1.6. Effect of limestone powder on hardened concrete

2.1.6.1. Effect of limestone powder on shrinkage

Autogenous shrinkage of concrete occurs during the hardening of concrete due to water absorption during the hydration of cement particles. Under the drying environment, moisture loss from the surface of hardened concrete results in drying shrinkage [2]. Limestone powder is less reactive than Portland cement and other active supplementary cementitious materials, it can be considered as an inert filler material do it can reduce shrinkage of concrete [29]. It was reported that the replacement of 10% cement with limestone reduced the total shrinkage of concrete by 19% [30]. In addition, the reaction of limestone powder and C3A in cement forms calcium carboaluminate and it increases the total volume of hydrate products [31]. Therefore, the incorporation of limestone powder reduced the chemical shrinkage of concrete. In this reaction, limestone powder acted as a reactant and mitigated the chemical shrinkage of concrete

[28]. The shrinkage of concrete decreased as the limestone powder content increased, as shown in Fig. 2.5 [32]. The incorporation of limestone powder reduced the cement content and increased the relative water to cement ratio, which increased the internal humidity of concrete and reduced the shrinkage of concrete [2].

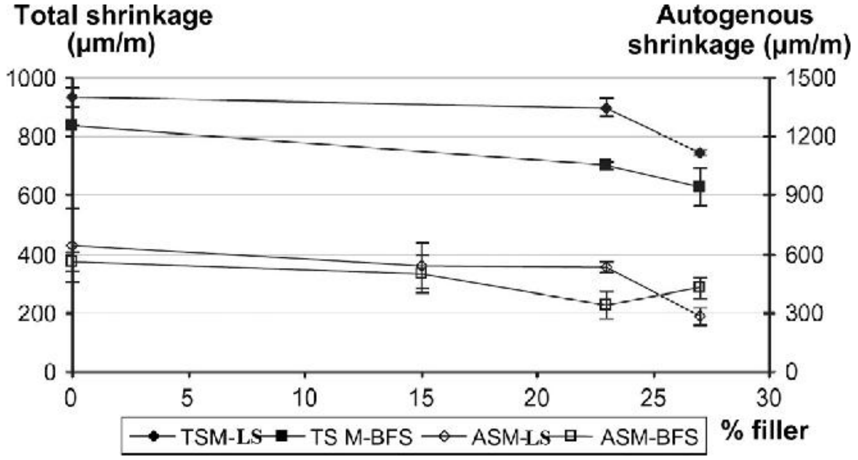


Fig. 2.5. Total and autogenous shrinkages of concrete after 28 days [32]

It is reported that when limestone powder is finer than cement particles, incorporating a small amount of limestone powder to replace cement acted as the nucleation sites which enhance the hydration process. Therefore, the incorporation of limestone powder could increase the autogenous shrinkage, as shown in Fig. 2.5.

2.1.6.2. Effect of limestone powder on microstructure

Generally, the incorporation of limestone powder can modify the microstructure of cement-based materials in different manners. Fine limestone powder could fill the pores between hydration products. The nucleation effect of limestone powder could improve the hydration process and form more hydration products. The chemical effect of limestone powder can increase the volume of the solid phase of hydration products. Therefore, all of these effects influence the microstructure of cement-based materials.

It is reported that the mean pore size of mortar with plain Portland cement was 60 nm in comparison with 31nm of mean pore size of mortar containing 10% limestone powder [33]. Incorporating proper fine limestone powder content reduced the volume of large pore and increased the volume of pores with a diameter smaller than 100nm [34,35]. In case of replacing aggregate with limestone powder, without a change in cement and water content, the threshold pore diameter of concrete containing limestone powder was lower than that of concrete without limestone powder, as shown in Fig. 2.6 [28]. In addition, the volume of large capillary pores and macro-pore of concrete containing limestone powder were less than that of concrete without limestone powder. incorporation of limestone powder to replace the aggregate filled the pores and reduced the porosity of mixtures [28].

The nucleation effect of limestone powder accelerated the hydration process, promoted the precipitation of C-S-H and filled the pores in the mixture at early ages [36,37]. In contrast, the dilution effect of limestone powder can occur when abundant coarse limestone powder was added into cement-based materials, the porosity of mixtures was higher than that of the control OPC mixture, as shown in Fig. 2.7 [38].

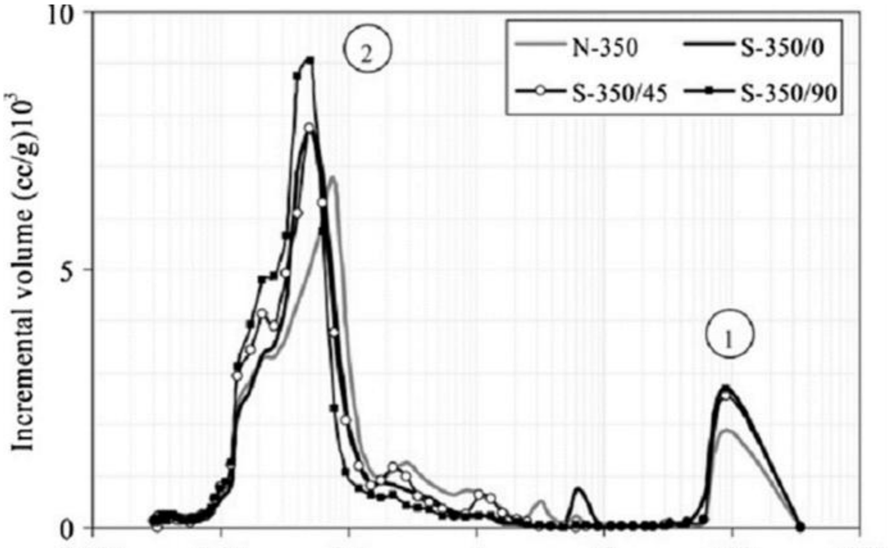


Fig. 2.6. Pore size distribution of mixtures with 350kg/m^3 of cement [28]

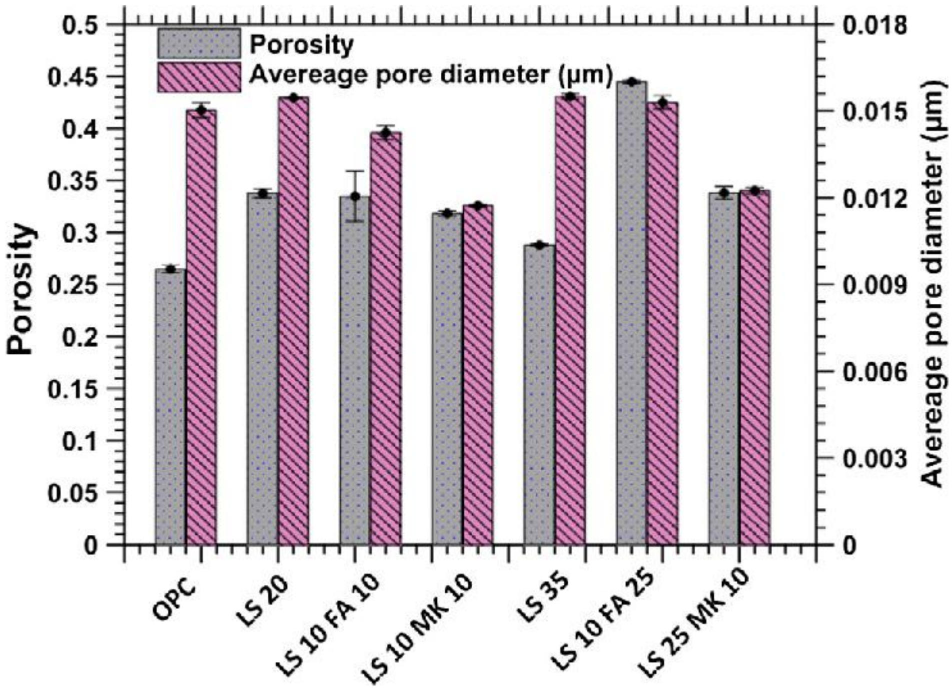


Fig. 2.7. Porosity and average pore size of blended binder pastes after 28 days of hydration [38]

2.1.6.3. Effect of limestone powder on mechanical properties

Compressive strength

Particle size, content and replacement pattern of limestone powder are factors that affect mechanical properties of concrete. Finer limestone powder could fill the void of cement particles and increase the packing density of cementitious materials. it is reported that the compressive strength of self-compacting concrete was improved because of the incorporation of ultra-fine limestone powder in concrete [39]. The compressive strength of concrete with fine limestone powder (5 μm) was larger than that of concrete with coarse limestone powder (10 and 20 μm) regardless of curing age [40].

When a large content of fine limestone powder replaced cement, limestone powder showed the dilution effect and resulted in the reduction of compressive strength of concrete. Generally, the compressive strength decreased as the limestone powder content increased [32,41] and the dilution effect of limestone powder was more pronounced at later age, as shown in Fig. 2.8 [42].

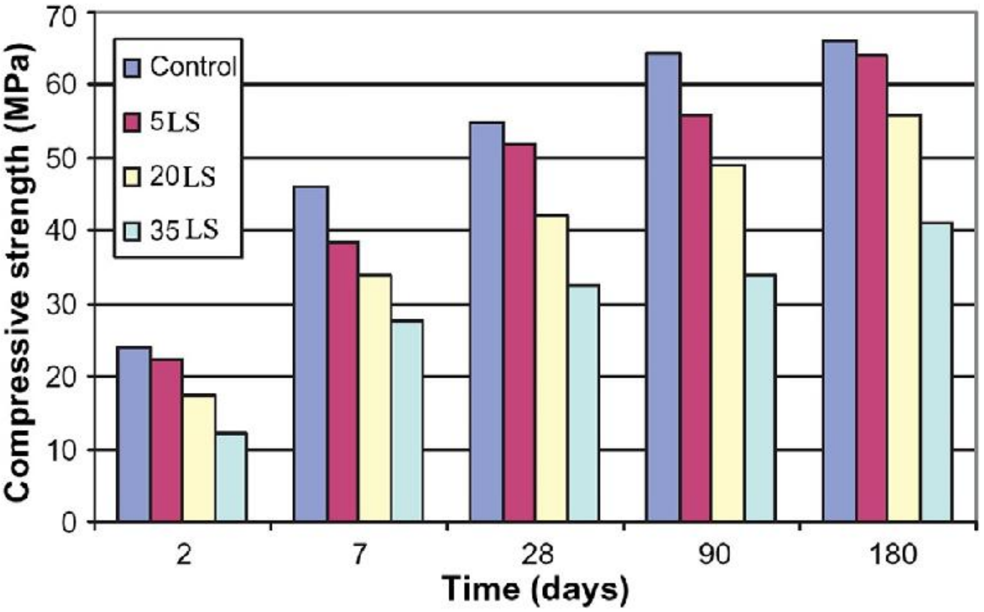


Fig. 2.8. Effects of limestone powder content on the compressive strength of mortars [42]

When limestone powder was used to replace cement or fine aggregate, it could fill the void of cement particles and aggregate and result in the increase of compressive strength. In addition, the incorporation of limestone powder promoted the precipitation of C-S-H and increase the hydration degree of cement due to its nucleation effect. On the other hand, the increase of powder and the decrease of water might reduce the bleeding of concrete, and thus improve the bond strength of the interfacial transition zones of concrete [43,44]. However, there was an optimum content of fine limestone powder used as the replacement of cement or fine aggregate. When the content of limestone powder is less than the optimum content, finer limestone powder shows the filler effect, while finer limestone powder mainly shows the dilution effect when the amount of limestone powder surpasses the optimum content [2]. It was found that incorporating no more than 5% limestone powder to replace cement increased the early compressive strength of concrete [45–47]. Likewise, Schmidt et al. [48] found that incorporating no more than 10% limestone powder to replace cement increased the compressive strength of concrete. Similarly, Li et al. [5] reported that when 3.0% nano-$CaCO_3$ was incorporated into ultra-high performance concrete (UHPC) to replace cement, the compressive strength of UHPC with W/B of 0.16 and 0.17 increased by 17% and 11%, respectively.

Elastic modulus

The incorporation of limestone powder to replace cement or fine aggregate could increase the elastic modulus of concrete. The elastic modulus increased as the limestone powder content increased [43,44]. Because limestone was stiffer than the cement matrix the elastic modulus of concrete increased by 9% when the limestone powder content increased from 25% to 100% replacement rate of fine aggregate for W/C of 0.6 and 0.47, respectively [43].

When limestone powder is used to replace cement, it can decrease the elastic modulus of concrete due to the dilution effect. It is demonstrated that the incorporation of limestone powder reduced the elastic modulus when fine limestone powder is used to replace 0-45% cement. The reduction in the elastic modulus ranged between 5-33% which was proportion to the limestone content. Using less than 15% limestone powder showed little effect on the elastic modulus of concrete while using more than 15% limestone powder to replace cement significantly reduced the elastic modulus of concrete [29].

Tensile strength

Incorporation of limestone powder for replacement of cement or fine aggregate could increase the tensile strength of concrete [43,44]. The tensile strength increased with the increase of limestone content in case of using limestone to replace fine aggregate [43]. When the limestone powder content increased from 25% to 100%, the tensile strength of concrete increased by 17% and 12% for W/C of 0.6 and 0.47, respectively [43].

Flexural strength

When limestone powder is used to replace cement, it mainly shows filler and dilution effects, and the nucleation and chemical effects of limestone powder on the flexural strength of concrete are not obvious [2]. Incorporating nano-limestone with a particle size of 15–80 nm to replace cement improved the flexural strength of UHPC [5]. The flexural strength of UHPC at W/B of 0.16 and 0.17 increased by 40% and 30% respectively when 3% nano-limestone was incorporated into UHPC to replace cement [5]. However, if the particle size of limestone was similar to cement, it would show the dilution effect. When limestone powder was used to replace cement, the content of cementing materials decreased while the non-cementing materials increased, which reduced the flexural strength of concrete. The flexural strengths reduced as the limestone powder content increased [45].

2.1.6.4. Effect of limestone powder on durability

Water permeability

It is reported that finer limestone powder can fill the voids of cement particles, reduce the porosity, and improve the water permeability of concrete [40,44,49]. Chen et al. [49] found that the water penetration depth significantly decreased as the limestone powder content increased, as shown in Fig. 2.9. It indicated that using limestone powder to replace 0–8% cement paste substantially decreased the water permeability of concrete, which could be attributed to its filler effect.

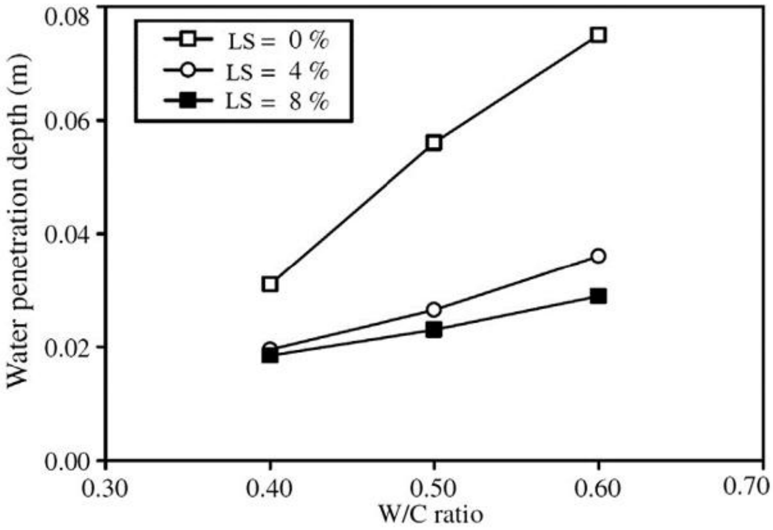


Fig. 2.9. Effects of limestone powder content on the water penetration depth of concrete [49]

When a large amount of limestone powder was used to replace cement, it showed filler, nucleation and dilution effects. There could be an optimum limestone powder content for the water permeability of concrete [41].

Sorptivity

It is reported that the incorporation of limestone powder to replace cement could reduce the sorptivity coefficient of concrete [49,50]. Chen et al. [49] found that adding limestone powder to replace 0–8 wt.% cement paste effectively reduced the sorptivity coefficient of concrete due to its filler effect, as shown in Fig. 2.10.

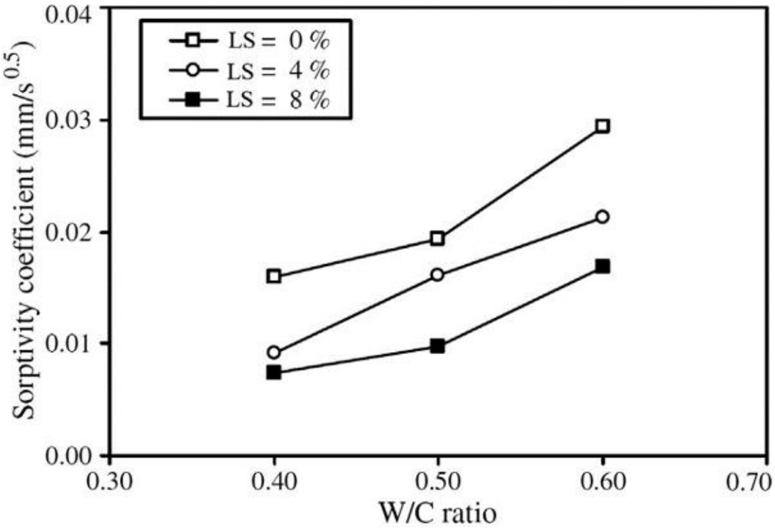


Fig. 2.10. Effects of limestone powder content on the sorptivity of concrete [49]

Chloride permeability

When appropriate content of fine limestone powder is added to replace cement, it mainly shows the filler effect and could reduce the chloride permeability of concrete. It was found that adding limestone powder to replace cement paste also reduced the chloride diffusion coefficient [44,51], as shown in Fig. 2.11 [44]. The pore structure of concrete was refined by incorporating limestone powder due to its filler and nucleation effects, thus, the chloride diffusion coefficient reduced as the limestone powder content increased fineness, especially when the amount of limestone powder surpassed 35% as shown in Fig. 2.12 [29].

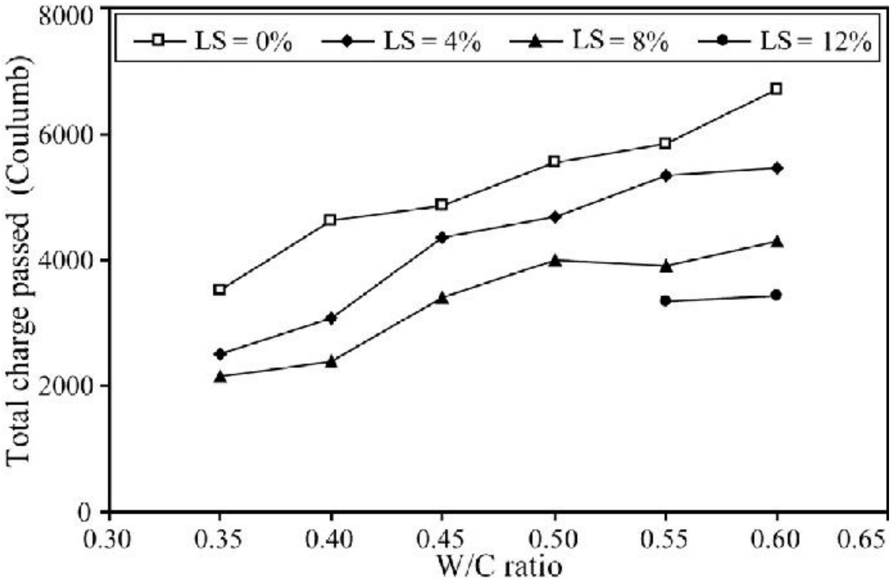


Fig. 2.11. Total charge passed versus W/C ratio in rapid chloride penetration test [44]

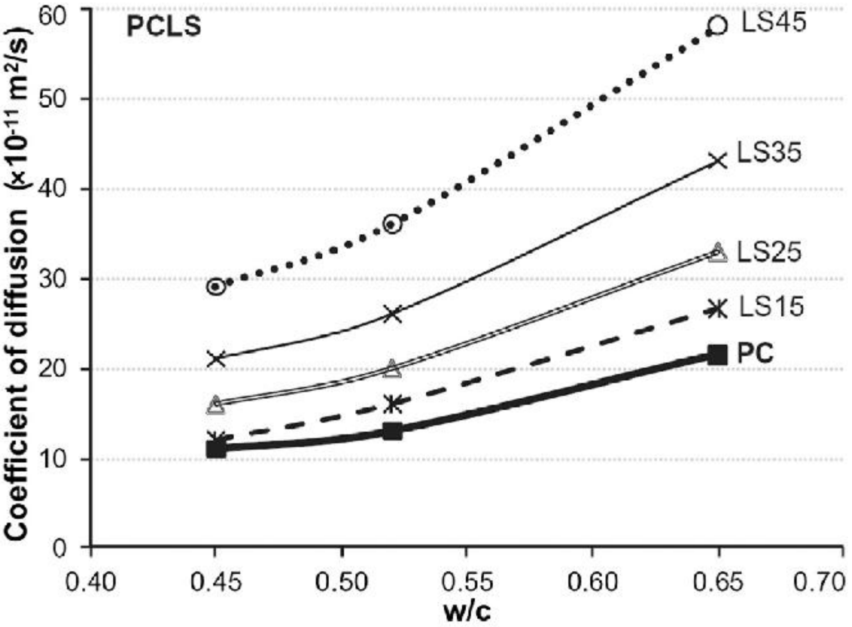


Fig. 2.12. Effects of different factors on the chloride diffusion coefficient of concrete [44]

Carbonation resistance

It is reported that adding limestone powder (Blaine fineness: 638 m2/kg) to replace 0–45 wt% cement significantly increased the carbonation depth of concrete, as shown in Fig. 2.13 [44]. The increase of carbonation depth might be attributed to the dilution and chemical effects of limestone powder which might consume CH in the reaction between limestone powder and aluminate phase. Parrot et al. [52] found that the natural carbonation depth increased when more than 19% limestone powder was added to replace cement. However, the weathering carbonation degree of concrete was slight when the limestone powder content was less than 15%. Compared with concrete containing fly ash or silica fume, the carbonation depth of concrete containing limestone powder was the highest. The reason could be the larger porosity of concrete containing limestone powder [53,54].

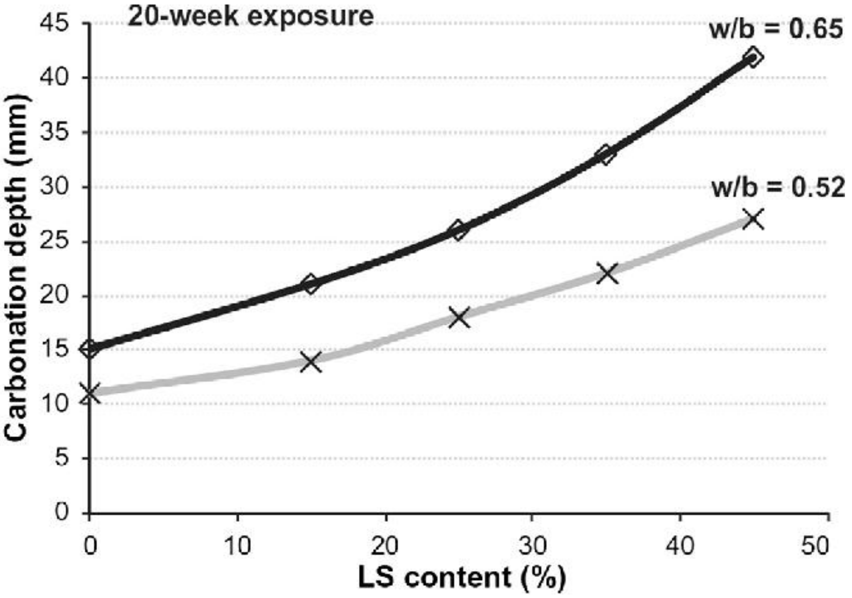


Fig. 2.13. Carbonation depth of concrete versus limestone powder content [44]

Corrosion resistance

The electrical resistivity of concrete influences its the corrosion resistance. As the electrical resistivity of concrete increases, the movement of electrons is retarded, thereby, the corrosion resistance of concrete is improved. It was reported that the electrical resistivity decreased with the increase of limestone powder content (Blaine fineness: 330 m^2/kg) [41]. Since the incorporation of 1% nano-limestone reduced capillary pores and C-S-H gels of concrete, it improved the corrosion resistance of concrete [55]. The better corrosion resistance of concrete containing limestone powder was also reported, which was accounted for the superior filler ability of limestone powder [56].

2.2. Effect of natural pozzolan on the properties of concrete

Mehta [57] classified natural pozzolan in four categories based on the identity of the pozzolanic constituents, namely siliceous and aluminous materials which in itself possess little or no cementitious properties, however in the presence of moisture will chemically react with calcium hydroxide at ordinary temperature to form cementitious compounds, as follows: unaltered volcanic glass, volcanic tuff, calcined clay or shale, and raw or calcined opaline silica.

2.2.1. Chemical and physical properties

Regarding chemical composition, many deposits contain SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, NaO, K_2O. In the most cased, the natural pozzolan is relatively high in silica compared to mineral crystals but relatively low in non- silica element (especially Mg and Fe); SiO_2 is the preponderant oxide (generally in range of 40-52% for basic lava, i.e. scoria and 63-75% for acid lava, i.e. pumice) [58–61]. Given their high silica content, natural pozzolan has a good acid resistance [62]. In a mixture of Portland cement and a pozzolan, the pozzolanic reaction progresses like an acid- base reaction between calcium hydroxide (CH) and alkalies with oxides (SiO_2+Al_2O_3+ Fe_2O_3) of pozzolan. Two phenomena occur in this mixture. First, there is a gradual decrease in the amount of free CH with time due to the consumption of CH in the pozzolanic reaction. Simultaneously, during this reaction, there is an increase of formation of C-S-H and calcium aluminosilicates and other products with low porosity that is similar to the hydration products of cement. This refinement of pores structure of cement-based materials resulted in the improvement of durability and chemical properties of concrete [57,63]

The shape, fineness, particle size distribution, density, and composition of natural pozzolan particles influence the properties of fresh concrete and hardened concrete. Most of natural pozzolans tend to increase the water requirement in the normal consistency because of their microporous character and high surface area.

Chemical and physical properties of natural pozzolan can be referred with ASTM C618-19, a standard specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete [64].

2.2.2. Reaction mechanism

The principal reaction is among amorphous SiO_2 and Al_2O_3 and CH derived from cement hydration in the presence of moisture (or water). This reaction forms additional cementitious gel C-S-H together with crystalline products, including calcium aluminate hydrates and aluminosilicate hydrates. Crystalline products depended principally on the amorphous phase of SiO_2, Al_2O_3/ CH ratio, and reaction temperature [65–67]. The pozzolanic reaction depends on the level of reactivity of natural pozzolan. Reactivity of natural pozzolan can be determined by the Chapelle test, and it expressed as a consumption rate of CH per gram of pozzolans [68–70]. Several techniques have been adopted to improve the pozzolanic reactivity of natural pozzolans, which include calcination [71–73], acid treatment [74,75], prolonged grinding [76,77], elevated temperature curing [78–80] and the use of chemical activators [81]. It has been found that the effect of calcination on the reactivity of the pozzolan depends on the combination of the two effects: an activation depending on the reactivity of the vitreous, zeolite and clay phase, and a deactivation depending on the decrease of specific surface area and soluble fraction and the increase of crystalline fraction [73]. Acid treatments result in the formation of gels on the surface of pozzolans and increase reactivity [74,75]; however, this technique is only suitable for low-calcium pozzolans [74]. Prolonged grinding of pozzolans and elevated temperature curing of concrete containing a natural pozzolan can increase reactivity, but their effects are minor. Often, concrete cured at elevated temperatures exhibits lower strengths at later ages. The addition of chemicals to concrete containing pozzolans can increase the pozzolanic reaction rate, strength development rate and ultimate strengths significantly. Although some chemicals such as caustic alkalis are very effective, they are expensive, dangerous and not practically feasible [82].

2.2.3. Effect of natural pozzolan on fresh paste/mortar/concrete

Workability

Because of their microporous character and high surface area, typically, natural pozzolan absorbs water from the mixture and holds this water in the system allowing improved finishing of concrete [83]. However, it can result in prolonged setting time and cause a reduction in the slump of concrete [84–86]. Hossain et al. [84] reported that normal consistency of blended cement paste containing volcanic ash (VA) and pumice powder (VP) decreased by 13.8% for VA and 12.4% for VP when the VA or VP content was varied from 0 to 50%. The normal consistency decreased by 3.79% when the VP content was increased from 0 to 25% compared to 5.17% in the case of VA. The decrease in normal consistency was due to the reduction of cementitious binder in the fresh mixture with the increase of VA or VP content. On the other hand, the overall volume was increased needing more water to form a paste of the same consistency for different percentage of VA and VP in the mixture. Shannang et al. [85] reported that there was a decrease in the flow of the mortar with the increase in pozzolan content. However, in some studies [83,87] the use of natural pozzolan together with superplasticizer can enhance the workability of concrete.

Natural pozzolans generally increase the cohesiveness of the mixture by producing a more plastic paste that allows the concrete to consolidate readily and flow freely under vibration. Increased cohesiveness also helps to reduce segregation [83].

Setting time

The use of natural pozzolan can extend the setting time of concrete especially in case of replacement of cement.

Hossain et al. [84] reported that the setting time of blended cement paste increased with the increase in the replacement of cement with volcanic ash (VA) and pumice powder (VP). This was reasonable as the decrease of cement in the mixture and also decreased the surface area of the cement. As a result, the hydration process slowed down, leading to an increase in the setting time. The setting-time characteristics of concrete are influenced by ambient and concrete temperature; cement type, source, content, and fineness; water content of the paste; water-soluble alkalies; use and dosages of other admixtures; the amount of pozzolan; the fineness and chemical composition of the pozzolan [83].

2.2.4. Effect of natural pozzolan on hardened concrete

2.2.4.1. Effect of natural pozzolan on the microstructure

E.Garcia et al. [88] examined the microstructure of hydration products of blended cement. Pastes of neat and blended Portland cement (incorporating either 60% ground granulated blast furnace slag, or 30% pulverized fuel ash, or 22% volcanic ash) were cured for one year at temperatures ranging from 10°C to 60°C . Microstructure of backscattered electron images (BEI) of the OPCS–VA blended cement after curing for 1 year at 10°C and 60°C are shown in Fig. 2.14. The microstructure observed after curing at 10°C indicated a high degree of hydration of the anhydrous phases in the cement and low porosity [89], whereas the porosity after curing at 60°C was appreciably greater. The apparent porosity of the pastes increased with increasing curing temperature. Chemical analysis data for the hydration products in ternary composition diagrams indicated that in the presence of the replacement materials the composition of the C–S–H shifted towards higher Si (from 0.31 for OPC to 0.35 for OPC–VA paste) and Al contents (0.031 for OPC to 0.045 for OPC–VA paste), whereas that of Ca was lower (0.66 for OPCS to 0.61 for OPCS–VA paste).

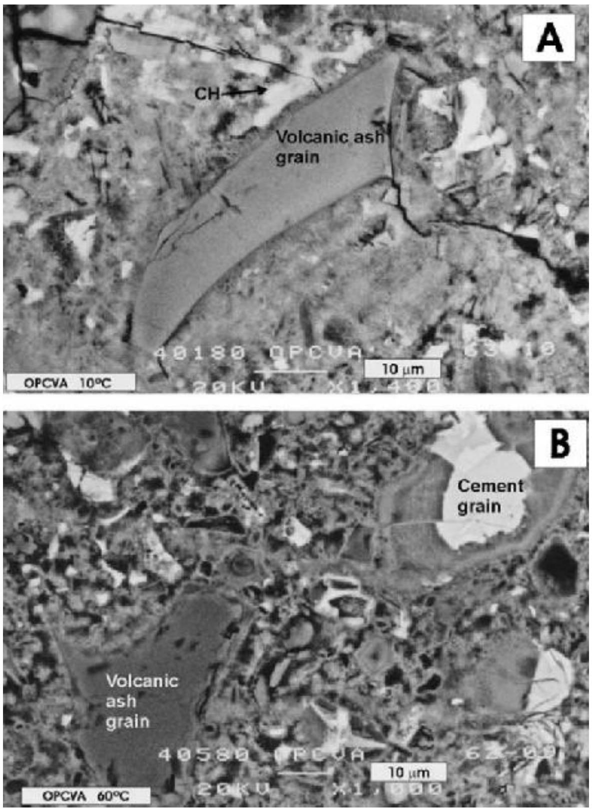


Fig. 2.14. BEI of OPCS-VA cured for 1 year at (A) 10ºC and (B) 60ºC [88]

Bredy et al [90] reported that when metakaolin content was below 20%, the total porosity of the paste decreased. Khatib et al. [91] found that the incorporation of metakaolin in cement paste led to refinement of the pore structure. The threshold value for paste decreased with the increase in metakaolin content (Fig.2.15). The proportion of pores with radii smaller than 20 μm increased with the increase in metakaolin content. Total intruded pore volumes increased between the ages of 14 and 28 days for metakaolin paste.

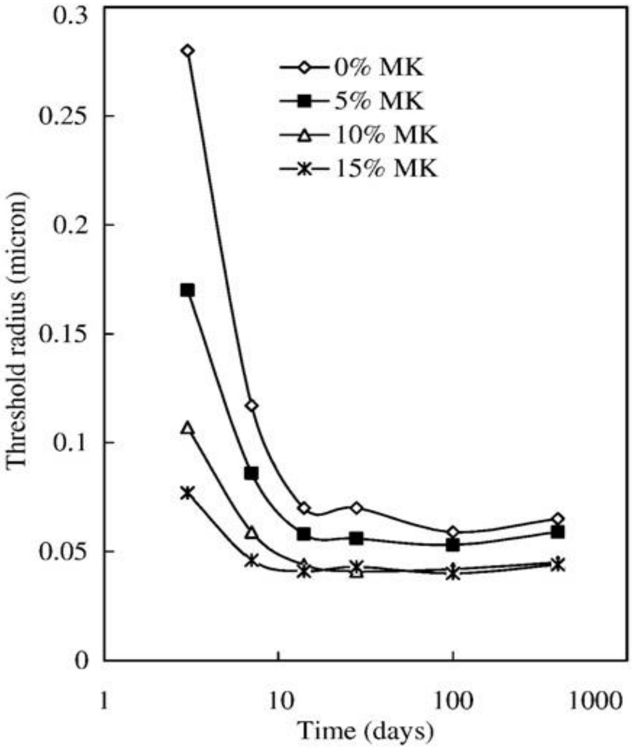


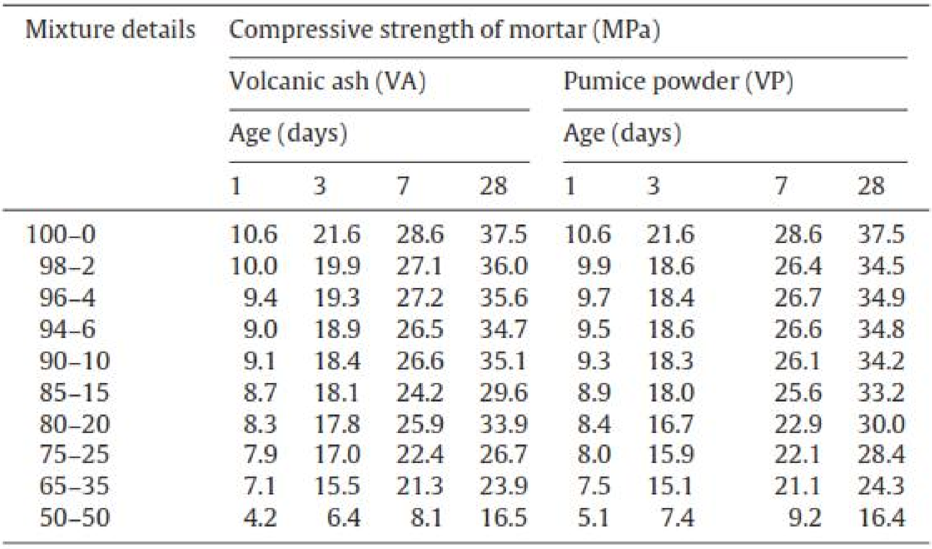
Fig. 2.15. Variation of threshold radius with time and metakaolin content [91]

2.2.4.2. Effect of Shirasu natural pozzolan on the mechanical properties

The effect of a natural pozzolan on the compressive strength of concrete varies markedly with the properties of the particular pozzolan and with the characteristics of the concrete mixture in which it is used.

Hossain et al. [84] studied the effect of partial replacement of cement with volcanic ash (VA) and pumice powder (VP) on the compressive strength of cement mortar. Percentage replacement varied from 0 to 50%. Tests were conducted up to the age of 28 days and results are given in Table 1. Based on the results, Hossain [84] concluded that compressive strength decreased with the increase in VA or VP content. This was due to the reduction of cement content in the mix with the increase of VA or VP content.

Table 2.1. Effect of volcanic ash and pumice powder on the compressive strength of cement mortar [84]



Mixture details	Compressive strength of mortar (MPa)							
	Volcanic ash (VA)				Pumice powder (VP)			
	Age (days)				Age (days)			
	1	3	7	28	1	3	7	28
100–0	10.6	21.6	28.6	37.5	10.6	21.6	28.6	37.5
98–2	10.0	19.9	27.1	36.0	9.9	18.6	26.4	34.5
96–4	9.4	19.3	27.2	35.6	9.7	18.4	26.7	34.9
94–6	9.0	18.9	26.5	34.7	9.5	18.6	26.6	34.8
90–10	9.1	18.4	26.6	35.1	9.3	18.3	26.1	34.2
85–15	8.7	18.1	24.2	29.6	8.9	18.0	25.6	33.2
80–20	8.3	17.8	25.9	33.9	8.4	16.7	22.9	30.0
75–25	7.9	17.0	22.4	26.7	8.0	15.9	22.1	28.4
65–35	7.1	15.5	21.3	23.9	7.5	15.1	21.1	24.3
50–50	4.2	6.4	8.1	16.5	5.1	7.4	9.2	16.4

Brooks et al. [86] reported that compressive strength increased with the increase in the metakaolin content (Table 2). Similar results were also reported by Li et al. [92] where concrete achieved the best compressive strength with 10% metakaolin content. Poon et al. [93] demonstrated that cement pastes containing 5% to 20% metakaolin had higher compressive strengths than the control at all ages from 3 to 90 days, with the paste containing 10% metakaolin performing the best. Jin and Li [94] concluded that the incorporation of metakaolin can improve both the strength and modulus of elasticity development of a young concrete, and metakaolin showed the best enhancement on the mechanical properties of young concrete.

Table 2.2. Compressive strength of metakaolin concretes [86]

Concrete mixes	Compressive strength (MPa)
OPC	87.0
MK5	91.5
MK10	104.0
MK15	103.5

Badogiannis et al. [95] studied the compressive strength of cement containing five metakaolins up to 180 days. The metakaolinite contents in metakaolins MK1, MK2, MK3, and MK4 (derived from poor Greek kaolins) were 36, 37, 71, and 49%, respectively, but 95% in a commercial metakaolin (MKC) of high purity. Metakaolin had a very positive effect on the cement strength after 2 days and specifically at 28 and 180 days. 10% of metakaolin content seemed to be, generally, more favorable than 20%.

Kaid et al. [96] reported that concrete using natural pozzolan as replacement of binder and fine aggregate exhibited improvement of mechanical properties of concrete after 28 days of cure

Table 2.3. Test result of compressive strength and elastic modulus of concrete [96]

	Curing time	RefPz	RefCem	ConPz
Compressive strength (MPa)	28	31.2 ± 2.4	33.3 ± 0.9	36.4 ± 2.4
	60	41.0 ± 1.9	44.5 ± 0.8	41.8 ± 1.7
	180	43.9 ± 1.6	45.7 ± 1.9	44.9 ± 0.6
	270	44.4 ± 0.6	46.0 ± 1.9	45.1 ± 0.5
Elastic modulus (GPa)	60	24.6	24.0	24.6

RefPz: Concrete with a binder composed of 80% CEM I and 20% NP was chosen as the reference Algerian concrete.

RefCem: Pozzolan-free concrete made of pure cement (CEM I)

ConPz: This concrete was designed to improve the durability of concretes with NP. It had the same binder as RefPz (80% CEM I – 20% NP), but with a supplementary quantity of NP added as sand replacement (13% of the mass of fine aggregate 0/0.315 mm)

2.2.4.3. Effect of Shirasu natural pozzolan on the durability

Alkali-silica reaction

Ramlochan et al. [97] reported that the incorporation of high-reactivity metakaolin (HRM) as a partial cement replacement between 10 and 15% may be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate. The mechanism by which HRM may suppress expansion due to alkali-silica reaction appeared to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions.

Water absorption and sorptivity

Courard et al. [98] indicated that water absorption of concrete mixtures increased with the increase in natural pozzolan content at 28 days and 14 months (Table 2.4). Khatib et al. [99] reported the increase in water absorption (WA) of concrete mixtures with the increase in natural pozzolan contents at all curing times (Fig. 2.16).

Table 2.4. Water absorption for mortar with cement CEM I, metakaolin and kaolin [98]

Material	Water absorption (% mass)	
	After 28 days	After 14 months
CEM I 42.5	8.16	7.82
5% metakaolin	8.39	8.04
10% metakaolin	8.78	8.44
15% metakaolin	9.71	8.77
20% metakaolin	9.70	8.97
10% kaolin	9.51	7.90

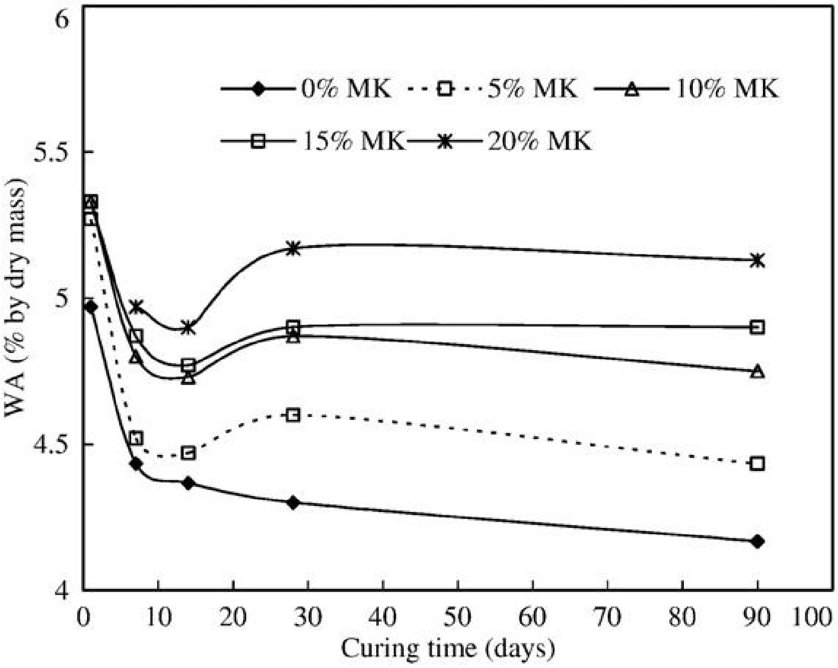


Fig. 2.16. Variation of water absorption of concrete containing metakaolin [99]

Chloride permeability

It is reported that concrete containing metakaolin showed significantly lower conductivity values than the Portland cement concrete [100]. Hooton et al [101] showed that 8 and 12% by mass of highly reactive metakaolin improved the chloride penetration resistance of both 0.30

and 0.40 w/cm concretes. Bai et al. [102] reported that significant reductions in chloride penetration depths were observed in the case of a partially replacement of cement with metakaolin in concrete exposed to seawater.

Poon et al. [103] investigated the chloride permeability of the concrete with metakaolin at w/b ratios of 0.3 and 0.5 were reported by (Table 2.5). Both the metakaolin concretes showed lower total ion penetration than the control concrete without any replacement of cement with mineral admixture. At w/b of 0.3, concrete with a 10% metakaolin showed the best performance, while at w/b of 0.5, 20% replacement was the best.

Table 2.5. Chloride permeability of blended concretes [103]

Series	w/b ratio	Mix	Total charge passed (Coulombs)			
			3 days	7 days	28 days	90 days
1	0.30	Control	2461	2151	1035	931
		5% MK	1327	1244	862	646
		10% MK	417	347	199	135
		20% MK	406	395	240	124
2	0.50	Control	5312	4054	2971	2789
		5% MK	4215	3765	2079	1065
		10% MK	1580	1247	918	752
		20% MK	751	740	640	580

Corrosion resistance, electrical resistivity

The use of metakaolin, either as a sand replacement up to 20% or as a cement replacement up to 10%, improved the corrosion behavior of mortar specimens, while there is an insignificant effect in case of metakaolin added in greater percentages [104].

The electrical resistivity is an indirect measurement of porosity and diffusivity. Hossain et al. [105] reported the results of the electrical resistivity of volcanic ash blended cement mortar. The mortars had 20% and 40% volcanic ash (VA) as cement replacement and water/binder ratio of 0.55. They pointed out that the electrical resistivity of the cement–VA mortars increased rapidly with the curing time. The 40%VA mortars had shown substantially higher resistivity than 20% VA mortars whereas the resistivity of the control mortar (0% VA) did not increase with the curing time especially in the long term and remained lower than the VA mortars. Electrical current through hydrating cement mortar is electrolytic (i.e., mainly due to the flow of ions through the pore spaces). It would enhance the overall resistivity of VA blended concrete and hence a lower degree of bar corrosion [105].

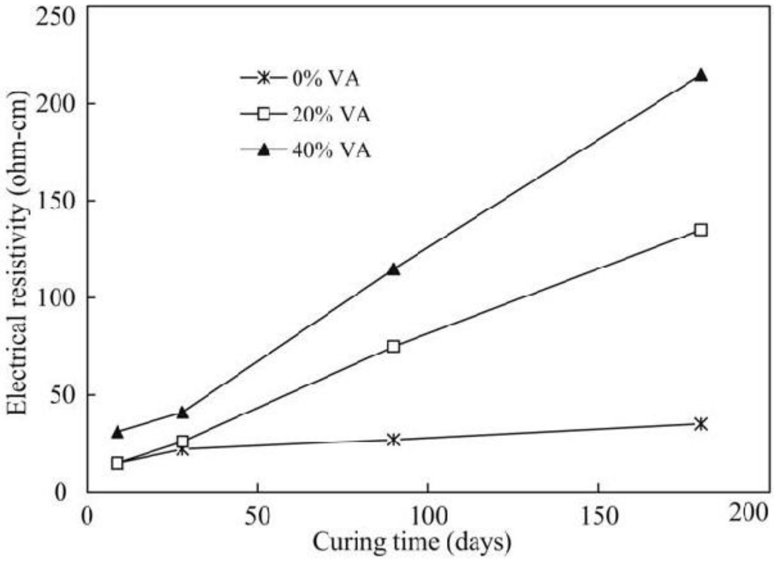


Fig. 2.17. Variation of electrical resistivity of concrete containing volcanic ash [105]

2.2.5. Shirasu natural pozzolan

Shirasu, a kind of the volcanic ash, which was abundantly deposited because of a huge pyroclastic flow covers a wide area of approximately 3500 km^2 in the southern part of Kyushu island, Japan, in 20 to 100 thousand years ago. Shirasu is sandy but porous material with a large amount of very fine particles. Fig. 2.19 showes microscopic of Shirasu which confirms the porous nature of Shirasu. It has about 80% density of that of sea sand and three times higher water absorption capacity when compared to sea sand. It also has a high quantity of volcanic glasses in its mineral compositions and has been confirmed to show the pozzolanic reactivity. The quantity of volcanic glasses in Shirasu`s composition is approximately 80% [106]. Therefore, it should be a potential construction material used as the replacement of binder, fine aggregate in mortar, concrete and geopolymer [107]. It is reported that Shirasu concrete has shown long-term durability concerning salt attack, sulfate attack, alkali-aggregate reaction, and etc. [108].

Fig. 2.18. Source of Shirasu [108]

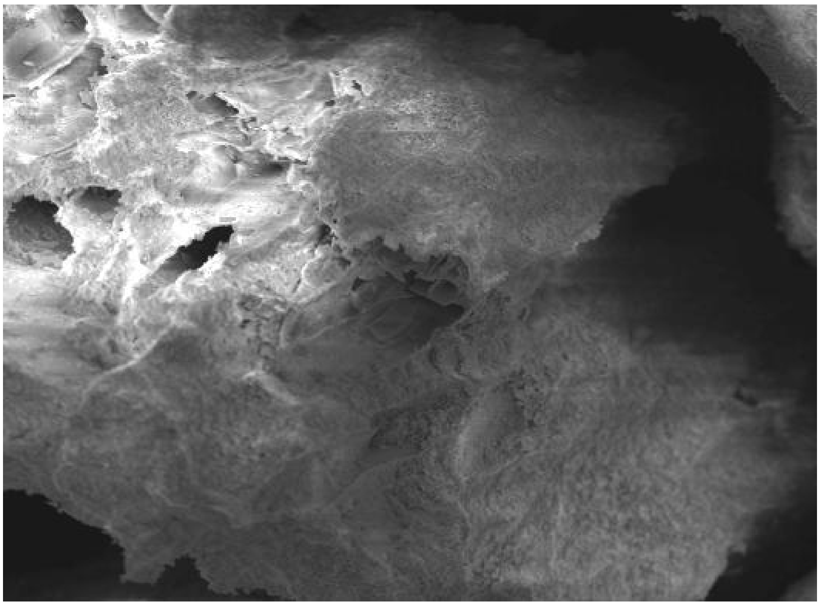


Fig. 2.19. Microscopic of Shirasu particle [108]

The different types of Shirasu deposits available in Kagoshima Prefecture of Japan at different locations based on density current and origin are shown in Table 2.6.

Table 2.6. Properties of different types of Shirasu [109].

Type of Shirasu/location	Density of surface-dry state (g/cm^3)	Absorption capacity ratio (%)	Fineness modulus	Fine powder ratio (%)
Kagoshima shi	2.06	11.31	1.53	21.9
Yoshida	2.22	4.29	1.57	20.54
Kiire	2.16	4.2	1.68	16.64
Makurazaki	2.24	3.11	1.18	23.4
Kaseda	2.16	8.48	1.12	27.55
Kawanabe	2.24	2.51	1.26	24.44
Higashi Ichiki	2.24	3.6	1.56	20.02
Koriyama	2.22	6.03	1.73	20.6
Ijuin	2.24	3.23	1.62	20.37
Matsumoto	2.22	3.07	1.63	24.46
Hioshi	2.24	2.67	1.6	21.3
Fukiage	2.19	4.29	1.43	26.63
Kimpo	2.22	3.07	1.14	19.48
Hiwaki	2.27	3.83	1.69	16.35
Tsuruta	2.25	3.61	1.44	26.41
Satsuma	2.23	3.82	1.52	24.06
Iriki	2.3	2.6	1.57	18.64
Izumi	2.22	5.07	1.21	25.52
Mizobe	2.16	6.4	1.83	17.91
Yokogawa	2.2	6.54	1.57	20.11
Kirishima	2.19	4.91	1.68	20.79
Fukuyama	2.11	9.62	2.09	20.86
Tarumizu	2.18	5.46	1.43	24.89
Takarabe	2.18	4.77	1.68	21.49
Shibushi	2.2	4.02	1.27	27.36
Sueyoshi	2.21	4.28	1.51	25.04
Matsuyama	2.24	3.11	1.5	24.53
Kihoku	2.17	3.62	1.87	22.35
Ariake	2.19	6.72	1.47	25.45
Takayama	2.19	4.17	1.5	23.36
Aira	2.17	2.88	1.37	24.8

2.3. Effect of curing temperature on properties of concrete

Many studies reported the effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes and pozzolanic activity of supplementary cementitious materials [110–114]. Based on a review of the references it is evident that the curing temperature significantly influences the mechanical properties and durability of concrete. Some experimental results [110,115] indicated that increasing the early age curing temperature tends to increase the compressive strength of concrete. This could be explained by the initial elevated temperature curing, which promoted the hydration reaction of cement and the pozzolanic reaction of the mineral admixture. However, some studies [114–116] demonstrated that at later-age the mechanical properties and durability of concrete are degraded with the increase of the early curing temperatures. Because the rapid hydration does not allow for sufficient time for the hydration products to diffuse within the voids and retards its further hydration. Therefore, the calcium silicate hydrates distribute non-uniformly and lead to a formation of large pores and a reduction in the strength of concrete. These behaviors had been called the crossover effect [117].

2.4. Deterioration of concrete in aggressive environment

2.4.1. Deterioration of concrete caused by acid environment

The aggressive acidic environment was derived from a variety of natural sources and industrial processes. In cases of free acids in industrial processes, the concentration of acid contacting with concrete structures may reach high values. The source of acid media can even represent air pollution by gaseous carbon dioxide, sulfur dioxide and nitrogen oxides. The acidic attack may also occur as a consequence of bacterial activity, leading to the formation of sulfuric acid in groundwater, sewage system or in the sulfate soil areas, etc. [118–121]. The acidic attack of cement-based materials is based on their alkalinity. If concrete structures are attacked by an acid, the components of the cement matrix, including calcium hydroxide and other hydration products, break down in accordance with the acid-base reaction. They are complex series of processes of decomposition and leaching of the constituents of the cement matrix. The decomposition and leaching of the cement-based materials depends on the porosity of concrete, on the concentration of the acid, the solubility of the acid calcium salts reaction products and on the fluid transport through the concrete (static condition or dynamic condition with change of level or flow of the acid solution)

[122,123]. Insoluble calcium salts may precipitate in the voids and can slow down the attack. Acids such as nitric acid, hydrochloric acid and acetic acid are very aggressive as their calcium salts are readily soluble and removed from the attack front. Other acids, such as phosphoric acid, are less harmful as their calcium salt, due to their low solubility, inhibits the attack by blocking the pathways within the concrete such as interconnected cracks, voids and porosity. Sulfuric acid is very damaging to concrete as it combines an acid attack and a sulfate attack [124]. The deterioration of concrete by the sulfuric acid attack can generally be characterized by equations (1)-(5), as follows [125] :

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O \qquad (2.1)$$

$$C_3S_2H_3 + 3H_2SO_4 + 4H_2O \rightarrow 3(CaSO_4.2H_2O) + 2(SiO_2.2H_2O) \qquad (2.2)$$

$$C_3AH_6 + 6H_2SO_4 \rightarrow 3(CaSO_4.2H_2O) + Al_2(SO_4)_3 + 6H_2O \qquad (2.3)$$

$$C_6AF_2H_{12} + 11\ H_2SO_4 \rightarrow 6(CaSO_4.2H_2O) + Al_2(SO_4)_3 + 2FeSO_4 + 11H_2O \qquad (2.4)$$

$$C_3AH_6 + 3(CaSO_4.2H_2O) + 14\ H_2O \rightarrow 3CaO.Al_2O_3.3\ CaSO_4.32H_2O \qquad (2.5)$$

The reaction products formed on the concrete surface are gypsum and possibly ettringite which are associated with the volume expansion, leading to tensile stress in concrete, cracking and spalling. It indicates that sulfuric acid attacked the cement matrix by decalcifying calcium hydroxide and hydration products and generating expansive reaction products, thus resulting in strength loss and crack occurrence in the concrete structure.

2.4.2. Deterioration of concrete caused by magnesium chloride

Magnesium chloride ($MgCl_2$) is commonly used in deicing applications due to its capability to depress freezing temperatures to a lower point than other salts such as sodium chloride (NaCl). However, it is reported that concrete exposed to $MgCl_2$ deicing salt typically exhibits changes in its microstructure due to chemical reactions, including formation of brucite $Mg(OH)_2$, Friedel's salts ($3Ca(OH)_2.\ CaCl_2.\ 10H_2O$), magnesium silicate hydrate (M–S–H), magnesium oxychloride ($Mg(OH)_2.MgCl_2.8\ H_2O$), and/or secondary calcium oxychloride

($3Ca(OH)_2 . CaCl_2 . 12H_2O$); these changes can result in severe cracking, even if the concrete does not experience any freezing and thawing cycles [126–129], as following equations:

$$\text{C-S-H} + MgCl_2 \rightarrow CaCl_2 + \text{M-S-H} \tag{2.6}$$

$$Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3Ca(OH)_2 . CaCl_2 . 12H_2O \tag{2.7}$$

$$MgCl_2 + 3Ca(OH)_2 . CaCl_2 . 12H_2O \rightarrow 3Ca(OH)_2 . CaCl_2 . 10H_2O + MgSO_4 .2\ H_2O \tag{2.8}$$

$$Ca(OH)_2 + MgCl_2 \rightarrow CaCl_2 + Mg(OH)_2 \tag{2.9}$$

$$(3 \text{ or } 5)Mg(OH)_2 + MgCl_2 + 8\ H2O \rightarrow Mg(OH)_2 .MgCl_2 .8\ H2O \tag{2.10}$$

It is reported that non-cementitious magnesium silicate hydrate (M-S-H) is formed by replacing the calcium from the cementitious calcium silicate hydrate (C–S–H), leading to the disintegration of cement matrix [130,131]. While the formation of calcium oxychloride has been reported to be very expansive and destructive within the cementitious matrix [127,129]. In contrast, the formations of, brucite, magnesium sulfate, and Freidel's salt are not generally reported as very destructive components.

2.4.3. Some methods of improving the resistance of concrete to aggressive environments

2.4.3.1. Type of cement

The type of cement used has also an important bearing on the performance of concrete in an aggressive environment [132]. It seems that high-alumina cement maybe show a high resistant to acidic attack solutions with pH values between 4 and 5. The better performance of these cement compared to that of Portland cement could be attributed not only to the absence of calcium hydroxide but to the presence of more stable calcium-aluminate hydrates in the cement matrix and also to the presence of aluminum hydroxide. This may encapsulate the hydration products and protect them from the acidic attack [133].

2.4.3.2. The incorporation of mineral admixture

The incorporation of mineral admixture is a common means of improving the resistance of concrete to the aggressive environment. Contradictory results have been reported with the replacement of cement with silica fume [134,135], blast furnace slag [136,137], fly ash [138,139], natural pozzolan [33,140–142]. Makhloufi et al. [143] 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 [144–146].

2.4.3.3. Water–cement ratio

It is known that the value of w/c ratio has a significant influence on cement hydration, microstructure and porosity of concrete structure. It is also known that the quality of concrete is increased with the w/c ratio decrease. The high w/c ratio used for composite mixtures will exhibit lower values of strength, bulk volume and higher porosity and potentially lower resistance to the aggressive environment [147,148]. Since one of the most important factors related to the mechanism of all the deterioration phenomena is permeability of concrete, while permeability of concrete is significantly influenced by w/c ratio. It is reported that the permeability is significantly reduced to a w/c ratio below 0.45. Therefore, in the interests of ensuring of an acid-resistant concrete, it is necessary that the w/c ratio should be less than 0.45 [132].

2.5. Summary

The incorporation of mineral admixture is a common means of improving the mechanical properties and durability of concrete. In addition, 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. In these environments, H^+, SO_4^{2-}, Mg^{2+}, Cl^- ions are considered as the most destructive ions for concrete structures. The deterioration of concrete caused by the attack of the mixed solution containing H^+, SO_4^{2-}, Mg^{2+}, Cl^- ions is a complex mechanism related to a series of physiochemical factors. However, very limited studies have examined the detrimental effect of these ions on the durability of concrete which associated with the service life and maintenance cost of civil infrastructure. Therefore, there is an urgent need to study the deterioration mechanism of concrete and identify means of improving the resistance of concrete to this aggressive environment.

For the aforementioned reasons, the effects of limestone powder and Shirasu natural pozzolan, abundant volcanic ash in Kyushu island of Japan, as fine aggregate replacements in concrete were investigated in this study with respect to the compressive strength development and the resistance of concrete to aggressive environment composing of sulfuric acid and magnesium chloride. In addition, the influence of initial curing temperature on the mechanical properties and the durability of concrete were investigated in order to determine the most effective curing conditions for concretes regarding technical and economic considerations.

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Chapter 3. EXPERIMENTAL PROGRAM

3.1. Introduction

This chapter presents the materials, mixture proportion, and experiments used in this study in detail. The physicochemical properties of limestone powder and Shirasu natural pozzolan, such as particle size distribution, the ignition loss, and density are mentioned in section 3.2. Section 3.3 explains the mixture proportion of various specimens.

Several experiments were conducted in the present study. Compression test was carried out to examine the compressive strength and the steady-state migration test to determine the chloride diffusion coefficient. The thermal analysis (TG-DTA) and chemical test were also carried out in order to determine the Portlandite ($Ca(OH)_2$) content of concrete mixtures under different curing temperatures. To investigate the deterioration mechanism of concretes caused by the aggressive environment, the immersion test was carried out. After 22 weeks of immersion, X-ray diffraction (XRD), compression test, erosion measurement, neutralization measurement and chloride penetration depth measurement were conducted. The concentration profile of ions was also established to determine the penetration level of SO_4^{2-}, Mg^{2+}, Cl^- ions in the concrete. Based on the experimental results, the mechanism of strength development and resistance of concrete to the attack of a mixed solution containing 3% H_2SO_4 and 5%$MgCl_2$ was investigated. The details of all these tests are explained in section 3.4.

3.2. Materials

The densities and chemical compositions of the cement, limestone powder and Shirasu natural pozzolan are presented in Table 3.1. 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 [1] 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) [2] was employed to achieve the desired workability for all concrete mixtures.

Table 3.1. 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

3.3. Mixture proportions

The mixture proportions and the fresh properties of the concretes are summarized in Table 3.2. 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 [4]. 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 [8]. Kaid et al. [8] 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. 3.1. 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) [9]. 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 3.2. 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

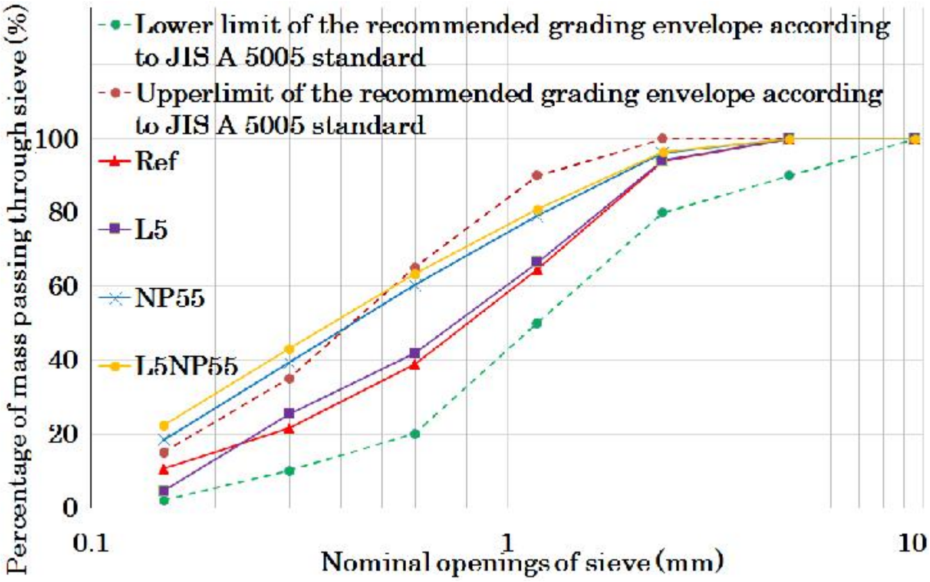


Fig. 3.1. Particle size distributions of the fine aggregate mixtures .

3.4. Test procedures and measurements

3.4.1. 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 investigating the deterioration of concrete after immersing in the mixed solution via X-ray diffraction analysis, erosion depth, neutralization depth, chloride penetration depth measurements and concentration profile of ions establishment. 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.

3.4.2. $Ca(OH)_2$ content

At ages of 3, 28 and 91 days, the $Ca(OH)_2$ content in the cement pastes of the concrete specimens was 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 [10] was adopted for the 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

$$CH = CH_1 \times 100 / C, \tag{3.1}$$

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

$$C = (m_s - m_r) \times 100 / m_s, \tag{3.2}$$

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

3.4.3. 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) [11].

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.

3.4.4. Chloride diffusion coefficient of concrete by steady-state migration test

The steady-state migration test [12,13] was adopted to find the diffusion coefficients of chloride ions in the concrete samples. Cylindrical concrete specimens with diameters of 100 mm and heights of 200 mm were fabricated and 30 mm thick slices were obtained from the center part of the specimens at the age of 91 days. The slice specimens were stored at 20°C and 60±5% relative humidity for 4 h prior to coating the circumference of each specimen with epoxy resin and installing each sample in the migration test apparatus shown in Fig. 3.2. To establish a steady state, the concentration gradient must be constant during the test. Therefore, the solutions in the anode and cathode sections were renewed when the chloride ion concentration in the anode section was higher than 0.05 mol/L or that in the cathode was lower than 0.45 mol/L, based on the JSCE-G571 standard (Test method for effective diffusion coefficient of chloride ion in concrete by migration) [13]. Consequently, the solutions in the anode sections were renewed after approximately 185 h of migration. Effective chloride diffusion coefficients for the L5, NP55 and LNP55 were determined based on three concrete discs while the value for the Ref mixture was obtained using two specimens because of limited experimental equipment. A voltage of 12 V was applied between the two sides of each concrete sample, although the actual measured potential was found to be approximately 10 V, and so this value was used when calculating the diffusion coefficients. All tests were carried out at 20±2 °C. The chloride concentration was measured by ion chromatography using a Dionex ICS-1000 instrument. The flux of chloride ions in the steady state was calculated using the equation

$$J_{Cl} = \frac{V}{A}\frac{\Delta C_{Cl}}{\Delta t}, \tag{3.3}$$

where J_{Cl} is the flux of chloride ions in the steady state (mol/m^{2}s), V is the volume of solution in the anode compartment (m^3), A is the cross-sectional area of the concrete sample (m^2) and

$\Delta C_{Cl}/\Delta_t$ is the increase in concentration of chloride ions in the anode (mol/m^3/s). The effective chloride diffusion coefficient was calculated using the equation

$$D_e = \frac{J_{Cl}RTL}{|Z|EFC_{Cl}}, \tag{3.4}$$

where D_e is the effective diffusion coefficient (m^2/s), R is the gas constant (8.3144 J/mol K), T is the absolute temperature (K), Z is the charge on a chloride ion (-1), F is the Faraday constant (96,480 J/V mol), C_{Cl} is the average chloride ion concentration in the cathode (mol/m^3), E is the electrical potential difference between specimen surfaces (V) and L is the length of the specimen (m).

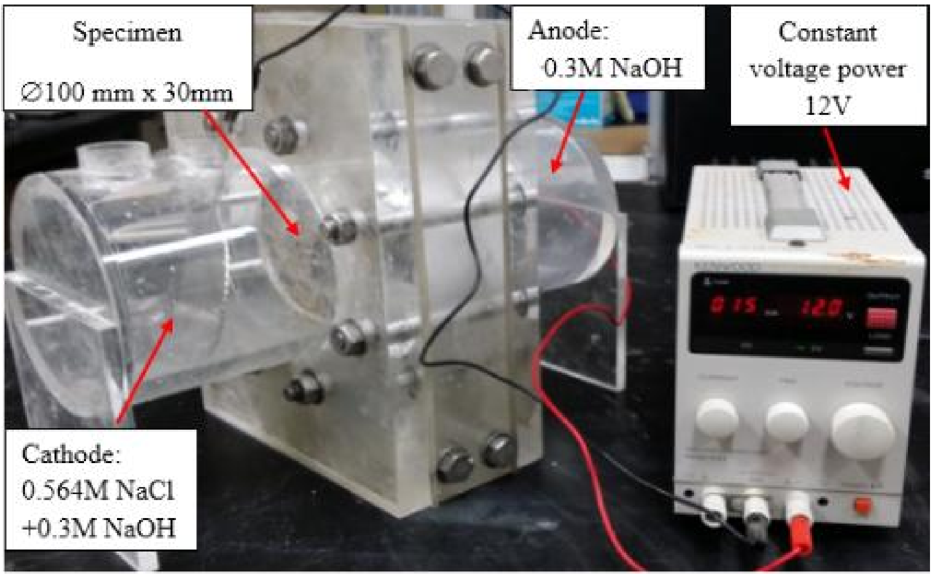


Fig. 3.2. The apparatus used for steady-state migration experiments.

3.4.5. Immersion test

3.4.5.1. 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.

3.4.5.2. X-ray diffraction (XRD) analysis

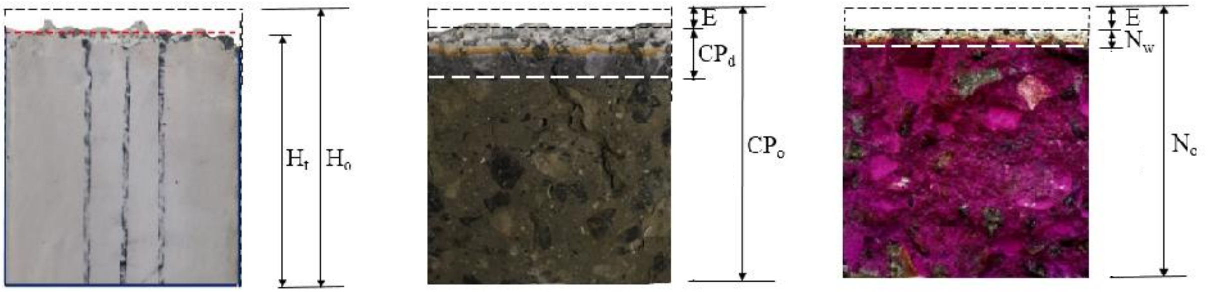
Dried powdered samples were extracted from the outermost layer of the surfaces of concrete specimens immersed in the mixed solution or in deionized water for 22 weeks. These powders were assessed by XRD to identify the primary crystalline phases, using an AXS D_2 Phaser X-ray diffractometer (Bruker Corporation).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

3.4.5.3. Erosion depth

A typical erosion depth measurement is shown in Fig. 3.3a. 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

$$\text{Erosion depth (mm)} = H_o - H_t, \tag{3.5}$$

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.



(a) (b) (c)

Fig. 3.3. Erosion depth (a), chloride penetration (b) and depth neutralization depth (c) measurements

3.4.5.4. Compressive strength loss

The ASTM C267-01 standard [14] (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

$$\text{Compressive strength loss (\%)} = (C_w - C_m) \times 100 / C_w, \tag{3.6}$$

where C_m is an average of three compression 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 compression test results for specimens immersed in deionized water for the same period of time (N/mm^2).

3.4.5.5. Neutralization depth

An example of the measurement of the neutralization depth of a sample after immersion in the mixed solution is presented in Fig. 3.3 (c). After being taken out of the solution and blotted with paper towels, each cubic specimen was cut into two at its center and the neutralization depth was detected by spraying the freshly split surface with a 1% phenolphthalein solution. The depth was ascertained at nine positions on the sample using an electronic caliper with 0.01 mm accuracy. The neutralization depth was then calculated using the equation

Neutralization depth (mm) = N_w+ E, (3.7)

where N_w is the depth of the uncolored zone after spraying with the phenolphthalein solution (mm) and E is the erosion depth determined using Equation (5) (mm).

3.4.5.6. Chloride penetration depth measurement

The chloride penetration depth of each specimen was measured by spraying silver nitrate 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 specimens. The chloride penetration depth was detected by spraying 0.1M silver nitrate solution on the freshly split surface of concretes. The chloride penetration depth was measured by using an electronic caliper with 0.01 mm accuracy. The chloride penetration depth determined by Equation (17) was calculated as the mean measured values of nine positions on the split surface of concretes.

Chloride penetration depth (mm) = CP_d + E (3.8)

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

E: erosion depth in Equation (5) (mm).

The measurement of chloride penetration depth of concrete immersed in the mixed solution was shown in Fig.3.3(b). In Fig.3.3(b), CP_o is the original depth of specimen before immersion in the mixed solution.

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

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. 3.4). In addition, slices were cut from the non-neutralized zone using an oil saw at 5 mm intervals, as shown in Fig. 3.4. 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 [15] and a previous report [16].

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.

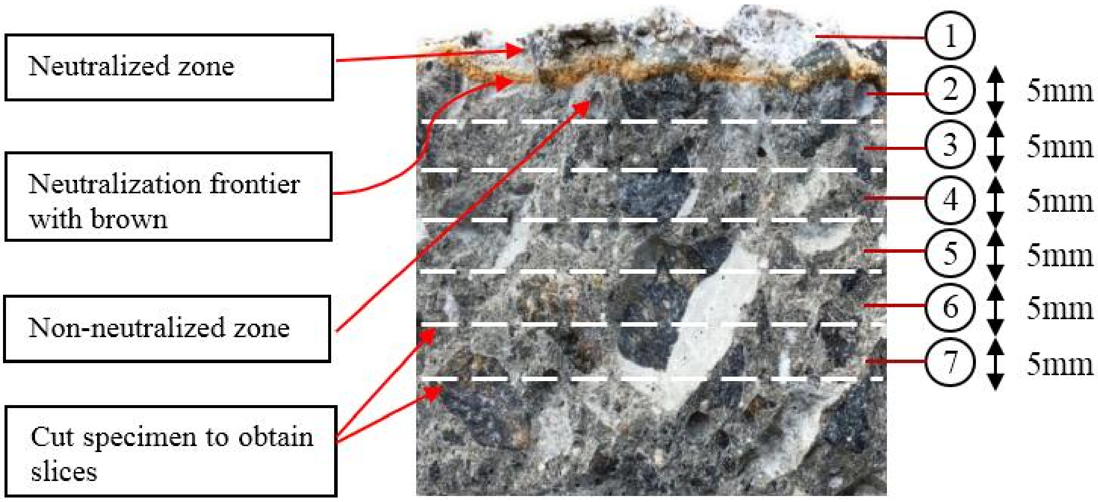


Fig. 3.4. Sampling of a deteriorated concrete specimen to measure Cl^-, SO_4^{2-} and Mg^{2+} ion concentrations

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Chapter 4. EFFECTS OF LIMESTONE POWDER AND SHIRASU NATURAL POZZOLAN ON THE STRENGTH DEVELOPMENT AND CHEMICAL RESISTANCE OF CONCRETE

4.1. Introduction

This chapter discusses the effects of limestone powder and Shirasu natural pozzolan on strength development and resistance of concrete to the attack of the mixed solution containing 3% sulfuric acid and 5% magnesium chloride which simulate the aggressive chemical environment. As mentioned in chapter 1, there are a few studies concerning the effects of limestone powder and natural pozzolan used as partial fine aggregate replacement on the strength development and resistance of concrete to the aggressive chemical environment containing H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions. While, H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions are considered to be the most destructive ions for concrete and can deteriorate its service life and increase the maintenance cost of civil infrastructures. Based on the experimental results, the effect of limestone powder and Shirasu natural pozzolan on the strength development and chemical resistance of concrete are analyzed and explained in this chapter. The deterioration mechanism of concrete caused by the attack of aggressive chemical environment containing H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions is also discussed.

4.2. Experiments

4.2.1. Mixture proportion

Four mixture proportion was produced by using limestone powder and Shirasu natural pozzolan as fine aggregate replacement. The proportions of fine aggregate replaced with the limestone powder and Shirasu were 5% and 55% by volume, respectively. A constant water/cement ratio of 0.40 and a cement content of 425 kg/m^3 were used for all concrete mixtures. The mixture proportions and the fresh properties of the concretes are summarized in Table 4.1. A reference concrete specimen (Ref) was made without replacing the fine aggregate.

Table 4.1. 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

4.2.2. Specimen preparation and curing condition

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

4.2.3. Test procedures and measurements

In this study, the thermal analysis (TG-DTA) and chemical test were also carried out in order to determine the Portlandite ($Ca(OH)_2$) content of concrete mixtures. To investigate the deterioration mechanism of concretes caused by the aggressive environment, the immersion test was carried out. After 22 weeks of immersion, X-ray diffraction (XRD), compression test, erosion measurement was conducted. The concentration profile of ions was also established to determine the penetration level of SO_4^{2-}, Mg^{2+}, Cl^- ions in the concrete. The details of these tests were mentioned in chapter 3.

4.3. Results and discussion

4.3.1. $Ca(OH)_2$ content

Figure 4.1 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) [1]. 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.

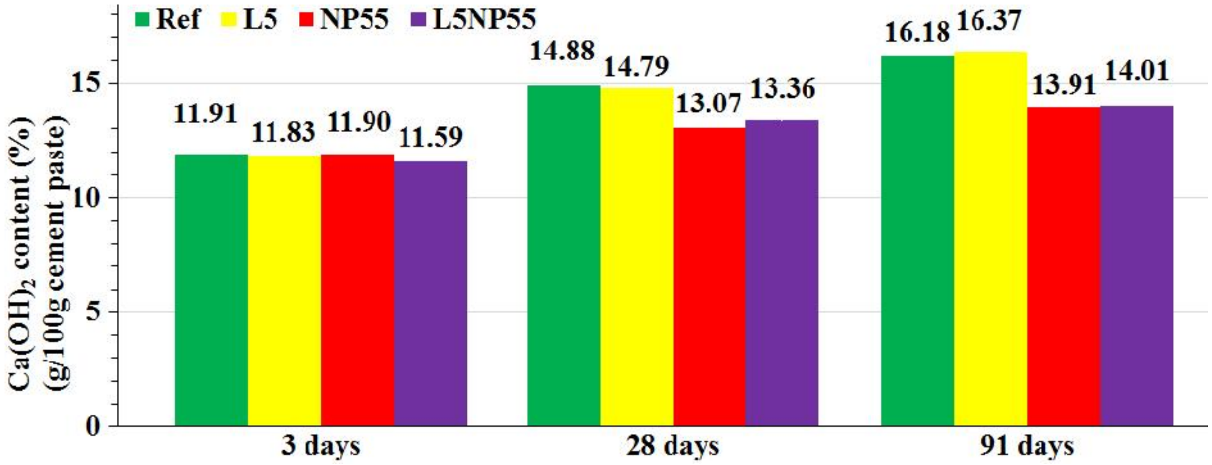

Fig. 4.1. $Ca(OH)_2$ content in concrete samples at different ages

4.3.2. Compressive strength

The compressive strengths of the concrete specimens at different curing ages are presented in Fig. 4.2. 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 [1–4]. 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 55% of fine aggregate replacement improved the compressive strength.

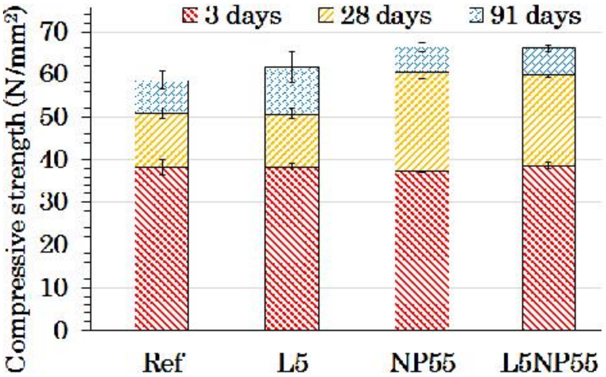

Fig. 4.2. Compressive strengths of concrete specimens after aging for 3, 28 and 91 days

4.3.3. Immersion test

4.3.3.1. 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. 4.3. 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 4.2. 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 [5–10].

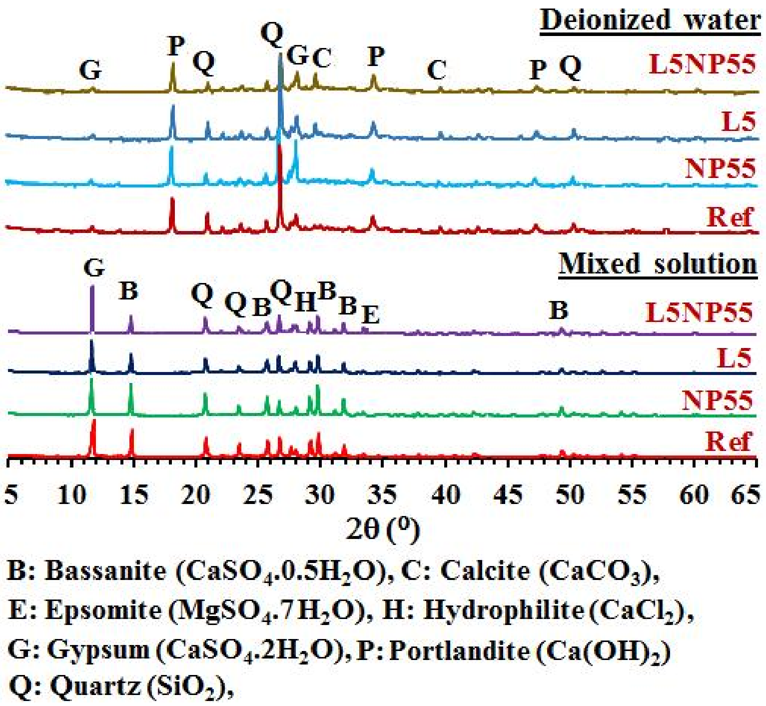

Fig. 4.3. XRD patterns of concretes immersed in the mixed solution or in deionized water for 22 weeks

Table 4.2. The main phases in concretes immersed in deionized water and the mixed solution detected by XRD method

Phase	Formula	Peak at 2θ	Remarks
Quartz	SiO_2	20.9°, 26.6°, 50.2°	
Gypsum	$CaSO_4.2H_2O$	11.7°, 20.7°, 29.1°	These peaks were more prominent in samples immersed in the mixed solution.
Bassanite	$CaSO_4.0.5H_2O$	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 mixtures cured in water and disappeared in all mixtures immersed in the mixed solution.
Calcite	$CaCO_3$	29.4°, 39.4°, 43.1°,	These peaks were more prominent in L5 mixture cured in water and disappeared in L5 mixtures immersed in the mixed solution.
Epsomite	$MgSO_4.7\ H_2O$	33.5°	This peak was only detected in samples immersed in the mixed solution.
Hydrophilite	$CaCl_2$	19.8°, 29.3°, 38.6°	This peak was only detected in samples immersed in the mixed solution.

4.3.3.2. Erosion depth

The erosion depths of specimens after immersion in the mixed solution are shown in Fig. 4.4. 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 [5–10]. 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 [11–13]. 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 [5,14]. Chatveera et al. [15] 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 [5,16].

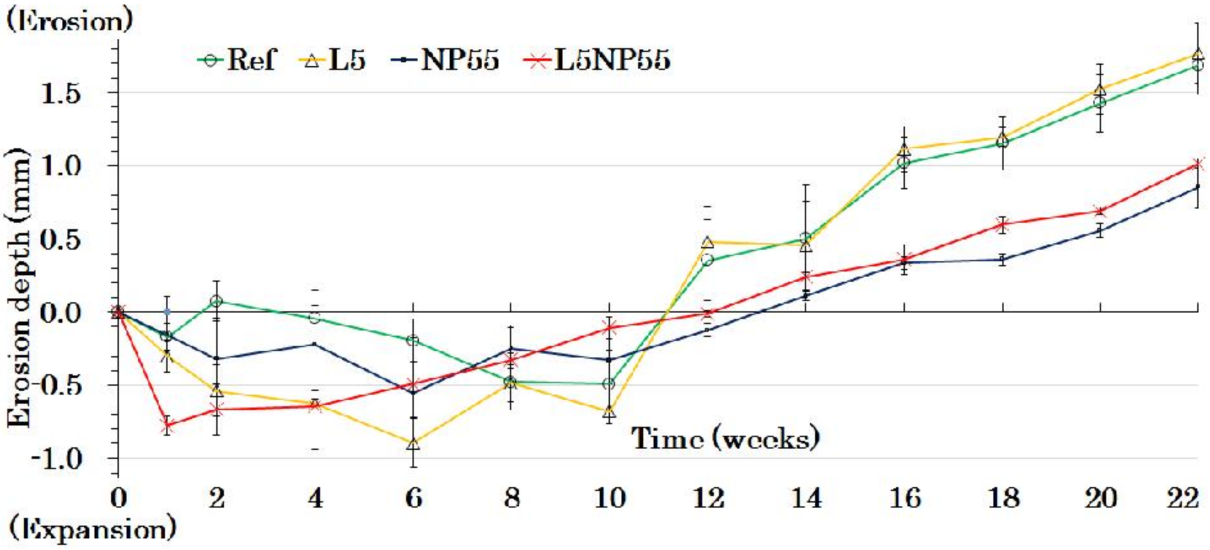

Fig. 4.4. Erosion depths of concrete specimens during immersion in the mixed solution

4.3.3.3. 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 4.3. 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 4.3.2).

Table 4.3. 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 4.5 shows the compressive strength losses of the concretes after 22 weeks of immersion in the mixed solution, as calculated using Equation (3.6). These data indicate that the highest compressive strength loss in the L5. In contrast, the best resistance to the aggressive chemical solution was found in the case of the NP55. The $Ca(OH)_2$ content of concretes had a major effect on the deterioration rate, which is associated with the residual strength [11–13]. 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. 4.1. 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 [1–4]. This microstructure refinement effect prevented the diffusion of 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 [17,18]. 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 [5–10]. This phenomenon leads to deeper diffusion of ions and thus an increased the deterioration rate of concrete.

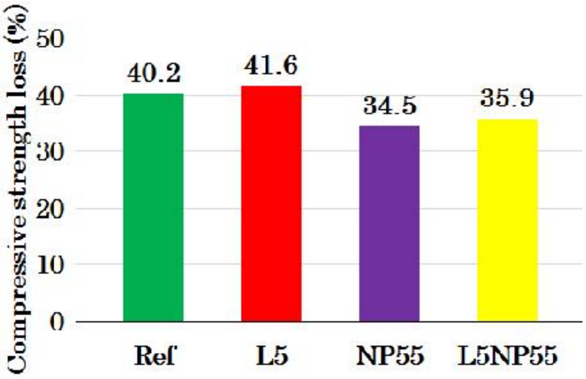

Fig. 4.5. Compressive strength losses of concrete specimens after 22 weeks of immersion

4.3.3.4. 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. 4.6, 4.7 and 4.8, respectively. According to Fig. 4.6, 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 4.7 and 4.8 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. 4 in chapter 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 [19–22]. Obserholster [19] reported that the diffusion of Cl^- ions is 10-100 times faster than that of SO_4^{2-} ions in concrete, while Stratful [21] determined that the diffusion rate of Cl^- ions was 14 times higher. Bakker [22] 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 4.

The results in Table 4.4 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 4.4. 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}

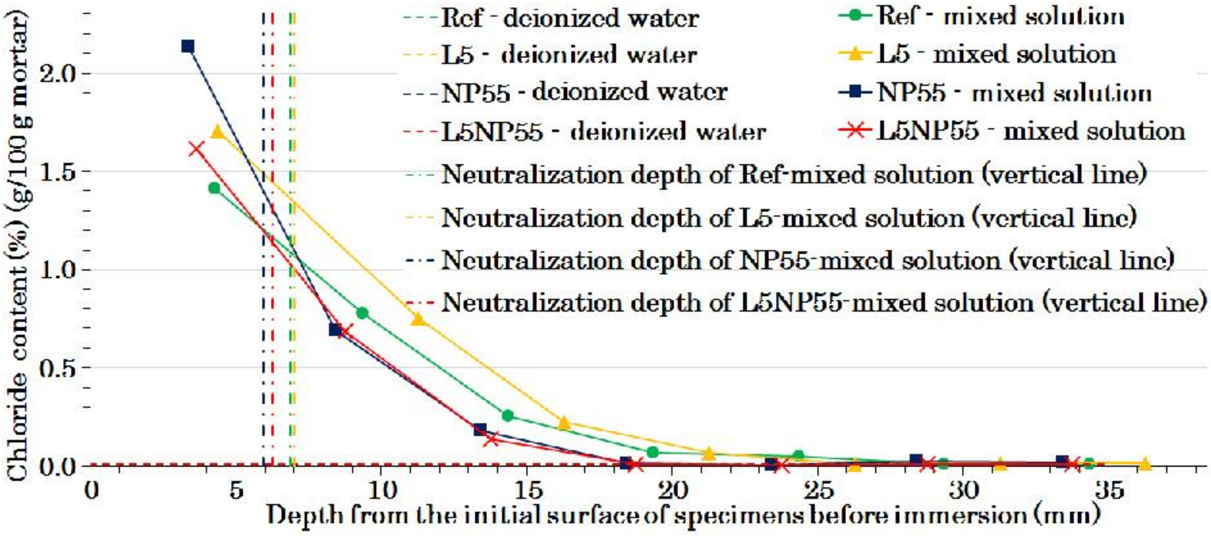

Fig. 4.6. The Cl^- ion penetration profiles in various concretes after 22 weeks of immersion

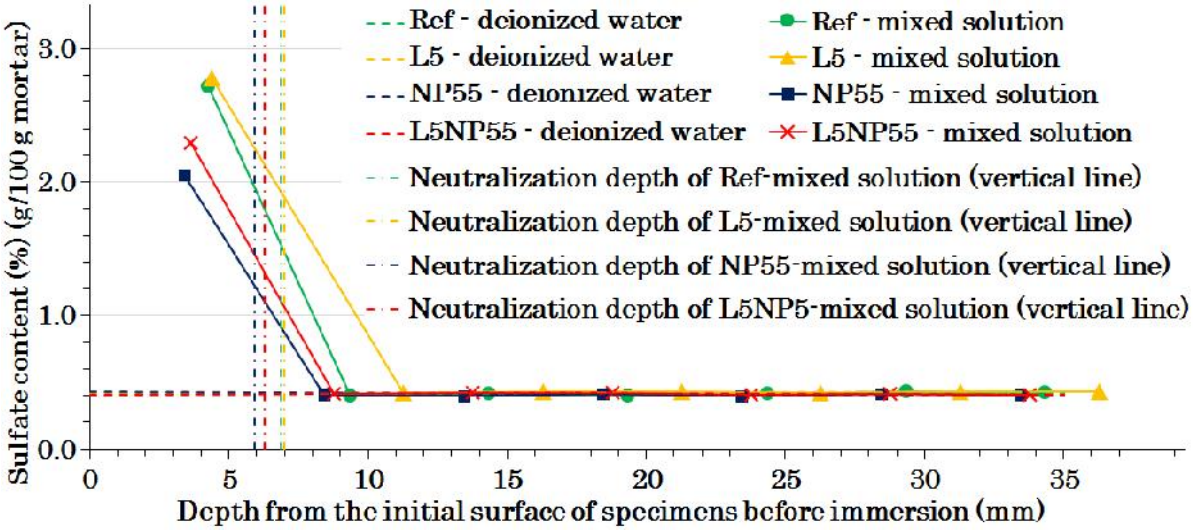

Fig. 4.7. The SO_4^{2-} ion penetration profiles in various concretes after 22 weeks of immersion

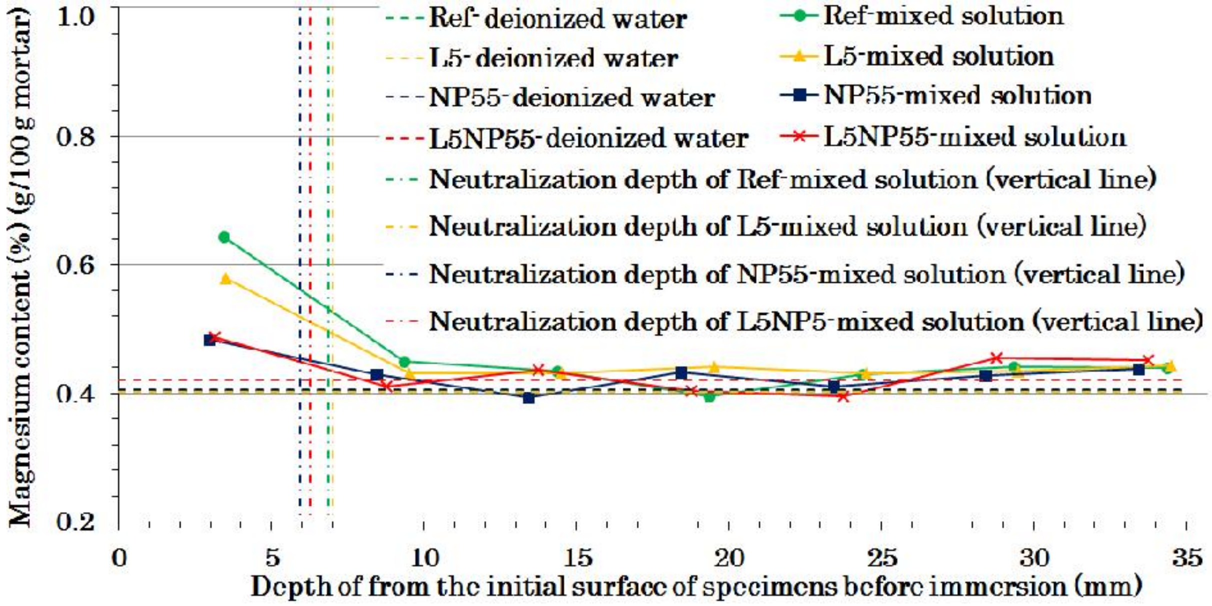

Fig. 4.8. The Mg^{2+} ion penetration profiles in various concretes after 22 weeks of immersion

4.4. Conclusions

This study analyses effects of limestone powder and Shirasu natural pozzolan on the strength development and chemical resistance of concretes in detail. The following conclusions can be drawn based on the mechanical and chemical analyses in this work:

- The usage of Shirasu as a fine aggregate replacement improved the compressive strength of concrete due to its pozzolanic reactivity.
- The effect of limestone powder on strength development was insignificant.

- The addition of Shirasu as a partial fine aggregate replacement improved the resistance of the concrete to an aggressive chemical solution containing 3% H_2SO_4 and 5% $MgCl_2$.
- The concrete using limestone powder as a partial fine aggregate replacement was suffered more severe deterioration of concretes by the aggressive chemical solution. However, the incorporation of the Shirasu compensated for this effect.

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Chapter 5. EFFECTS OF INITIAL CURING TEMPERATURE ON THE STRENGTH DEVELOPMENT AND CHEMICAL RESISTANCE OF CONCRETE CONTAINING LIMESTONE POWDER AND SHIRASU NATURAL POZZOLAN

5.1. Introduction

This chapter discusses the effects of initial curing temperature on the compressive strength development and chemical resistance of concrete containing limestone powder and Shirasu natural pozzolan. As mentioned in chapter 1, many previous studies reported that curing temperature significantly influence the hydration process of cement as well as the pozzolanic reaction [1–6]. However, there are a few studies concerning effects of initial curing temperature on the compressive strength development and chemical resistance of concrete containing limestone powder and Shirasu natural pozzolan to the aggressive chemical environment containing H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions. While, 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. Based on the results of the experimental results, the effect of initial curing temperature on the compressive strength development and chemical resistance of concrete containing limestone powder and Shirasu natural pozzolan was analyzed and explained.

5.2. Experiments

5.2.1. Mixture proportion

Three mixture proportion was produced by using limestone powder and Shirasu natural pozzolan as fine aggregate replacement. The proportions of fine aggregate replaced with the limestone powder and Shirasu were 5% and 55% by volume, respectively. A constant water/cement ratio of 0.40 and a cement content of 425 kg/m^3 were used for all concrete mixtures. The mixture proportions and the fresh properties of the concretes are summarized in Table 5.1. A reference concrete specimen (Ref) was made without replacing the fine aggregate.

Table 5.1. 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	39	337	303	1005	10.0±2.0	9.5	2.0±0.5	2.0

5.2.2. Specimen preparation and curing condition

Two types of specimens were produced: one was cylindrical specimens of 100 mm diameter and 200 mm height for compression tests and other was cubic specimen with the size of 100×100×100 mm for other tests. After casting, specimens of each concrete mixture were separated into two groups: one was applied for normal curing temperature condition in which specimens were cured in a sealed condition with aluminum tape at 20°C until the designated test ages (i.e., 3, 28, and 91 days for the compressive strength measurements); whereas the other was placed under sealed condition with aluminum tape at high curing temperature history of 60°C for 8 hours followed by cooling process in the curing chamber. The schematic of heat treatment regime which was referred to the curing temperature history of the previous studies [3,4,7] is shown in Fig. 5.1. In the previous studies, this heat treatment regime was applied for investigating the effects of steam curing on the properties of self-compacting concrete containing limestone powder which is used in the precast concrete plant [3] and recycled aggregate fly ash concrete [4,7]. In the study, this method was considered also for examining the effect of initial curing temperature on the properties of concrete containing Shirasu natural pozzolan and limestone powder in this study. After the initial curing stage of 24 hours, the specimens were cured under sealed condition with aluminum tape at 20°C until the designated test ages

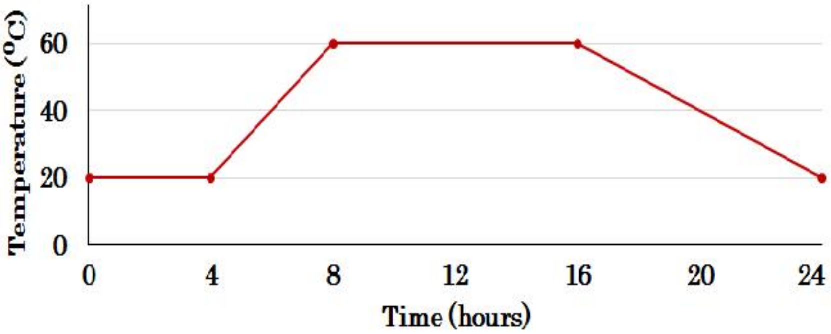

Fig. 5.1. Schematic representation of the heat treatment procedure

5.2.3. Test procedures and measurements

In this study, the compression test was conducted for determination of strength development of concrete. The thermal analysis (TG-DTA) and chemical test were also carried out in order to analysis the Portlandite ($Ca(OH)_2$) content of concrete mixtures. To investigate the chloride resistance of concrete, the steady-state migration test [8] was adopted to find the chloride diffusion coefficients. The deterioration mechanism of concretes cured at different initial curing temperatures caused by the aggressive environment was also studied. The immersion test was carried out. After 22 weeks of immersion, X-ray diffraction (XRD), compression test, the measurement of erosion depth, neutralization depth, chloride penetration depth was conducted. The detail of these tests was mentioned in chapter 3.

5.3. Results and discussion

5.3.1. $Ca(OH)_2$ content

Figure 5.2 shows the $Ca(OH)_2$ content of concrete samples cured at different temperatures. It can be seen that under normal curing temperature, the $Ca(OH)_2$ contents in concretes containing Shirasu (NP55) substantially reduced at the ages of 28 and 91 days in comparison with that in concretes without Shirasu (Ref and L5). It is assumed that the consumption of $Ca(OH)_2$ owing to the pozzolanic reaction between Shirasu and $Ca(OH)_2$ led to lower $Ca(OH)_2$ content in the concrete containing Shirasu than that in concretes without Shirasu.

The $Ca(OH)_2$ content in NP55 was significantly lower than that in Ref cured at high temperature condition regardless of the ages. Especially, at the age of 3-day curing, the $Ca(OH)_2$ contents in concretes containing Shirasu (NP55) was almost equal to that of concrete without Shirasu under normal curing temperature, however, at the same time under high curing temperature, the $Ca(OH)_2$ contents of NP55 was significant lower than that of Ref and L5 concretes. It can be inferred that elevated temperature can promote the pozzolanic reactivity of Shirasu, which accelerates the consumption of $Ca(OH)_2$ at the early ages.

In addition, the use of limestone as fine aggregate replacement insignificantly affected the hydration process of cement pastes regardless of the curing temperature. As a result, the $Ca(OH)_2$ content of L5 was almost identical to that of Ref regardless of curing temperature conditions at different curing ages.

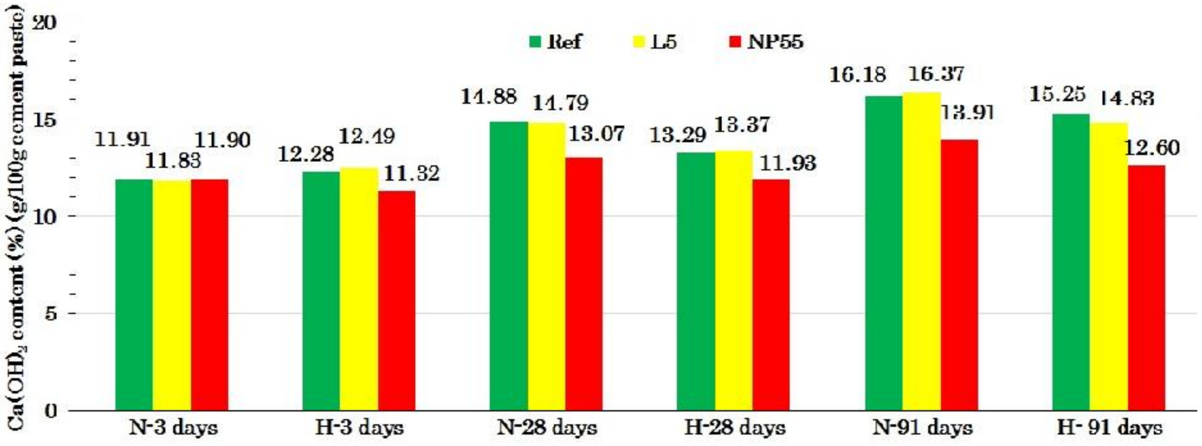

Fig. 5.2. $Ca(OH)_2$ content in cement pastes of concretes cured at different curing temperatures: N - normal curing temperature; H - high curing temperature

5.3.2. Compressive strength

The compressive strength of concrete specimens at different curing ages is illustrated in Fig. 5.3. It can be observed that under normal curing condition, at the age of 3 days, the compressive strength of concrete containing Shirasu (NP55) is almost the same as those of concrete without Shirasu (Ref and L5). However, at the later age, the compressive strength of NP55 is significantly higher than that of concrete without Shirasu after 28 and 91 days under normal curing temperature conditions. Considering the results of the $Ca(OH)_2$ content as shown in Fig. 5.2, it can be said that the pozzolanic reaction between Shirasu and $Ca(OH)_2$ produced additional cementitious hydration products, namely calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H) and refined the pore structure of cement matrix [9], leading to the strength development of concretes. Furthermore, Fig. 3 also shows that under high curing temperature condition, the compressive strength of concrete containing Shirasu (NP55) moderately exceeds those of concretes without Shirasu (Ref and L5) at the age of 3 days. It indicates that initial high curing temperature can promote the pozzolanic reactivity of Shirasu, leading to the formation of additional cementitious hydration products and the increase of the compressive strength of concrete containing Shirasu at the early age. Considering the results of the $Ca(OH)_2$ content as shown in Fig. 2, at the age of 3 days, under high curing temperature condition, the $Ca(OH)_2$ content of concrete containing Shirasu was significantly lower than those of concretes without Shirasu due to the pozzolanic reactivity of Shirasu.

In the case of L5 concrete, the effect of limestone powder on the compressive strength of concrete was insignificant. The strength of L5 was almost the same as that of Ref regardless of curing temperatures.

In addition, the compressive strength at early age (i.e., at the age of 3 days) of concretes cured at high temperature was higher than that of concretes cured at normal temperature. On the other hand, the later-age compressive strength of all concrete mixtures cured at high temperature condition were less than that of concrete cured under normal curing condition after 28 and 91 days of curing. This result agreed with the previous studies [10–12]. It is reported that concrete exposed to elevated temperature shows accelerated cement hydration, leading to the increase in compressive strength of concrete at the early age. However, more precipitated hydration products that quickly deposited may form a barrier for further ion diffusion and hydration process, resulting in inhomogeneity of microstructure and significant strength reduction of concretes at the later age [10,11].

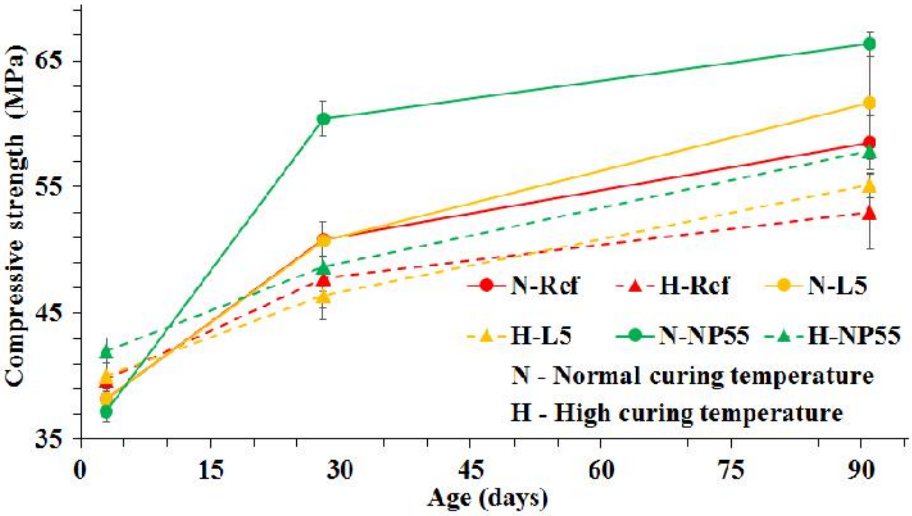

Fig. 5.3. Compressive strengths of concrete specimens after aging for 3, 28 and 91 days.

5.3.3. Chloride diffusion coefficient

Figures 5.4 and 5.5 show the total increase of chloride concentration in the anode solution over time and the chloride diffusion coefficient of mixture proportions, respectively. It indicates that the lowest rate of chloride diffusion was recorded for concretes containing Shirasu (NP55) regardless of curing temperature condition, followed by the rate of chloride diffusion of L5. Ref concrete without replacing the fine aggregate showed the highest rate of chloride diffusion. Obviously, the addition of Shirasu improved the resistance of concrete to chloride permeability because pozzolanic reaction led to the formation of additional cementitious material which contributed to refinement pore structure and the reduction of interconnection of pores [13]. This result also agreed with the report of [14] on the resistance of concrete using Shirasu as fine aggregate to the chloride-induced deterioration during 3 years of immersion in the tidal sea zone. In addition, using limestone powder as fine aggregate replacement also reduced the chloride permeability of concretes. It can be explained that the filling effect of limestone powder in the voids between aggregates and cement grains could result in the densification of concrete structure and contribute to impede the diffusion of ions from external environments into concretes.

Furthermore, the effective chloride diffusion coefficients of concretes cured at normal temperature were lower than those of concretes cured at high temperature, as seen in Fig. 8. It is assumed that higher porosity of concretes cured at high temperature [11,15] resulted in higher chloride permeability than that of concretes cured at normal temperature. Detwiler et al. [16] also reported that elevated curing temperatures result in coarser pore structure and a corresponding decrease in the resistance to chloride ion diffusion.

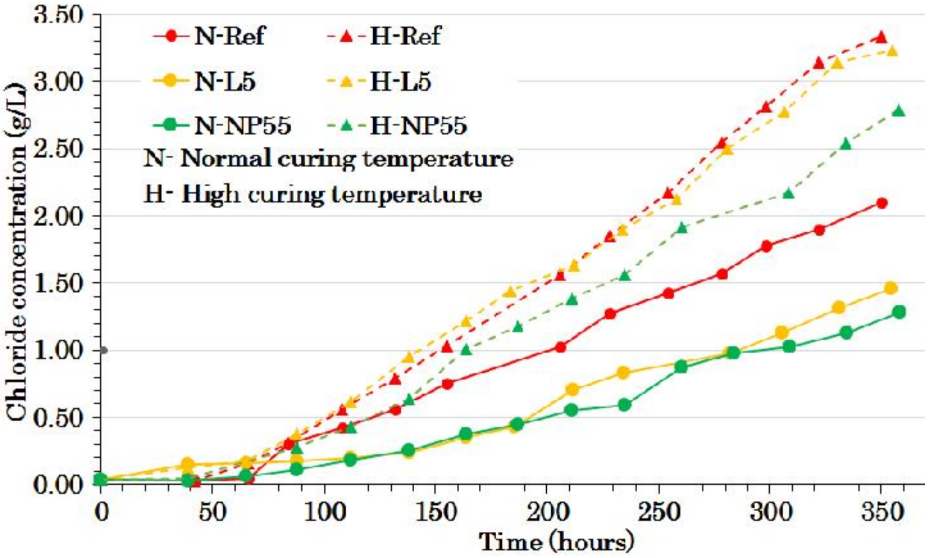

Fig. 5.4. Cumulative increase of chloride concentration in anode sections.

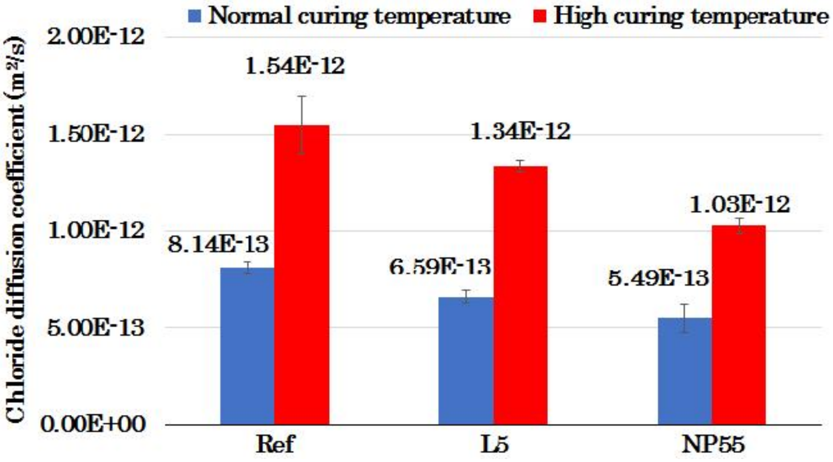

Fig. 5.5. Chloride diffusion coefficients of concretes

5.3.4. Immersion test

5.3.4.1. XRD analysis

Figure 5.6 shows the patterns of the major peaks detected by the XRD test in the specimens immersed in the mixed solution and pure water. It indicates that all samples immersed in deionized water showed prominent peaks for the main phases of portlandite ($Ca(OH)_2$). However, it can be seen that no peak of $Ca(OH)_2$ was observed in the patterns of concrete immersed in the mixed solution. In addition, high peaks of calcite ($CaCO_3$) appeared in L5 sample immersed in water. Nevertheless, $CaCO_3$ peaks disappeared from all patterns of concretes immersed in the mixed solution. It indicates that $Ca(OH)_2$ and $CaCO_3$ are most susceptible to react with the mixed solution containing sulfuric acid and magnesium chloride. The presences of high contents of $Ca(OH)_2$ and $Ca(OH)_2$ were responsible for more severe deterioration of L5 concrete than other concretes immersed in the mixed solution. In addition, prominent peaks of bassanite ($CaSO_4.0.5H_2O$), gypsum ($CaSO_4.2H_2O$), hydrophilite ($CaCl_2$) and epsomite ($MgSO_4.7\ H_2O$) observed in the XRD patterns of all concretes immersed in the mixed solution confirmed the formation of these reaction products caused by attack of the mixed solution. These products are non-cementitious materials which lead to strength loss of concrete structure. In addition, reaction products such as gypsum ($CaSO_4.2H_2O$) associated with volume expansion could precipitate and fill in the pores of concrete structure, leading to the internal stress and crack in concrete structure, eventually [17,18].

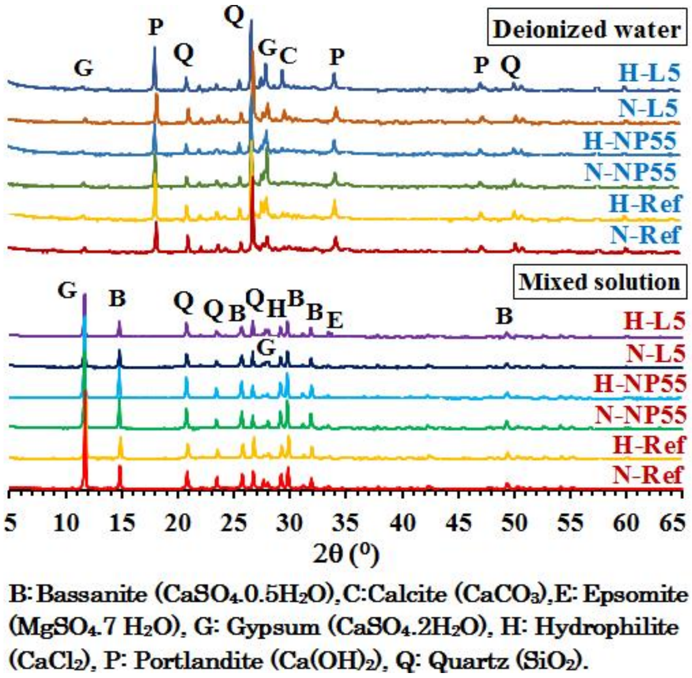

Fig. 5.6. XRD patterns of concretes after 22 weeks of immersion in water and mixed solution. Name of specimens labelled with N - normal curing temperature; H - high curing temperature.

5.3.4.2. Erosion depth

The erosion depths of specimens immersed in the mixed solution is shown in Fig. 5.7. In the Fig. 5.7, a negative value of erosion depth implies the expansion of specimen while a positive value of erosion depth indicates the erosion of specimen. The results show that the expansion process was almost observed during the initial 10 weeks of immersion in the mixed solution for all mixtures. After 12 weeks, the erosion significantly occurred in cases of Ref and L5 concretes. while, the NP55 showed a slight erosion. In addition, after 22 weeks, the erosion depths of concretes containing Shirasu (NP55) were lower than those of Ref and L5 regardless of curing temperature conditions. It indicates that the addition of Shirasu mitigated the erosion of the concretes immersed in the mixed solution. Considering the XRD results, the generation of chemical reaction products, including gypsum ($CaSO_4.2H_2O$), bassanite ($CaSO_4.0.5H_2O$), epsomite ($MgSO_4.7\ H_2O$), hydrophilite ($CaCl_2$) was confirmed. It implies that the occurrence of expansion was attributed to the formation of reaction products such as gypsum ($CaSO_4.2H_2O$) which is usually associated with volume expansion of concretes [20–23].

However, long-term immersion, concrete was decomposed by aggressive chemical reaction between the mixed solution and cementitious materials, leading to serious erosion. The decomposition of concrete structure can be confirmed by the evolution of reaction products such as gypsum ($CaSO_4.2H_2O$), bassanite ($CaSO_4.0.5H_2O$), epsomite ($MgSO_4.7\ H_2O$), hydrophilite ($CaCl_2$).

The lower erosion depth of concrete containing Shirasu in comparison to that of concrete without Shirasu may be attributed to lower $Ca(OH)_2$ content which is available to react with sulfuric acid and magnesium chloride. Furthermore, the addition of Shirasu natural pozzolan may influence on the chemical resistance of concrete. Detwiler et al. [24] pointed out that the C-S-H produced by pozzolanic reaction has a denser structure and calcium-to-silicate ratio lower than conventional C-S-H produced by OPC hydration. It was also pointed out that the lower C/S ratio and $Ca(OH)_2$ content contribute to reduction of acidic deterioration rate of concrete [20,22,23].

Moreover, the erosion depth of concretes cured at high temperature was lower than that of concretes cured at normal temperature because of lower $Ca(OH)_2$ content as seen in Fig. 2. In addition, the precipitated deposition of chemical reaction products in the voids of concrete structure acted as a barrier to slow down the attack of aggressive chemicals [17,20,25]. It is assumed that the concretes cured at high temperature have higher porosity [1,12,26] leading to the larger precipitated reaction products in the pore structure as a barrier to reduce the deterioration rate of concretes cured at high temperature in comparison with that of concretes cured at normal temperature.

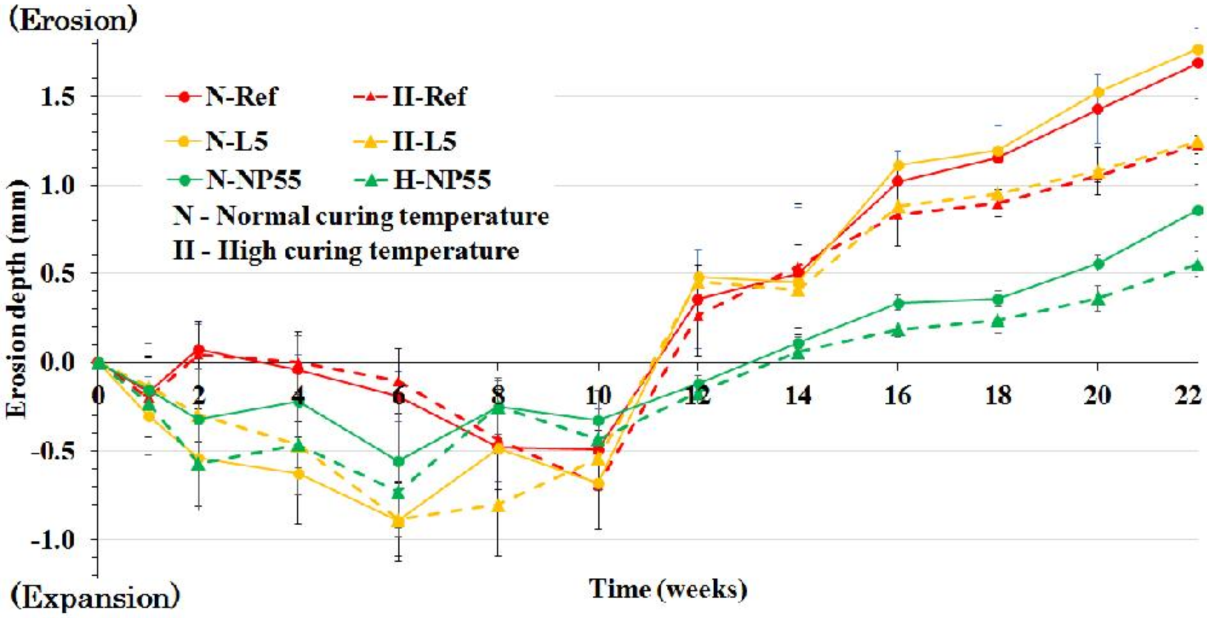

Fig. 5.7. Erosion depth of concrete after 22 weeks of immersion in the mixed solution.

5.3.4.3. Compressive strength loss

After 22 weeks of immersion in the mixed solution, the residual compressive strength of the specimens was determined. The compressive strength of concrete specimens immersed in the mixed solution and deionized water for a period of 22 weeks are listed in Table 3. It can be seen that the residual compressive strength of concrete containing Shirasu (NP55) was higher than that of other mixtures without Shirasu (Ref and L5) at the same immersion period regardless of the curing temperature.

Figure 5.8 shows the compressive strength loss of concretes after 22 weeks of immersion in the mixed solution. It indicates that the highest compressive strength loss was recorded for the mixture containing limestone powder (L5). In contrast, the lowest compressive strength loss was found to be in NP55 compared to other concretes in both curing temperature conditions. The reason for the higher resistance of NP55 in comparison with the other concretes may be the lower $Ca(OH)_2$ content, which is the most vulnerable to aggressive chemical attack. On the other hand, L5 contained high amounts of $Ca(OH)_2$ and $CaCO_3$ which were vulnerable to chemical reaction as mentioned in the XRD analysis, resulting in the highest compressive strength loss. In addition, the pozzolanic reaction of Shirasu resulted in the formation of additional calcium silicate hydrate (C-S-H) and calcium aluminum silicate hydrate (C-A-S-H) [9]. The additional hydration products lead to refinement effect of the pore structure, including reduction in interconnectivity of the pore structure [27]. The refinement effect prevented the diffusion of H^+, SO_4^{2-}, Mg^{2+} and Cl^- ions into the concrete structure.

Moreover, after the 22-week immersion, the strength loss of all concretes cured at normal temperature was considerably higher than that of specimens cured at high temperature conditions. Regarding the mechanism of concrete deterioration caused by attack of a high concentration of sulfuric acid solution at pH degree less than 1, previous studies reported that sulfuric acid reacts with cement hydration products to produce expansive reaction products such as gypsum, leading to increase in volume of solid substances which causes expansion, internal stress and cracks in the concrete structure [17,18]. In addition, concrete with higher amount of larger capillary pores showed higher absorption capacity of expansion derived from the deposition of reaction products, leading to less severe micro crack-induced deterioration than that with lower amount of large capillary pores [28,29]. It was reported that after immersion in high concentration of sulfuric acid solution, more cracks can be occurred in concretes with lower W/C ratio associated with lower porosity than in concretes with higher W/C ratio.

For the aforementioned reasons, including lower $Ca(OH)_2$ content and higher expansion absorption capacity associated with less cracks in concrete structure, the concretes cured at high temperature showed a lower deterioration rate than the deterioration rate of concretes cured at normal temperature.

Table 5.3. Compressive strength of concrete specimens after 22-week immersion in deionized water and the mixed solution and the standard deviation of compressive strength values (S.D.)

Curing condition	Mixture	Compressive strength (N/mm^2)			
		pure water	S.D.	mixed solution	S.D.

Normal temperature	N-Ref	64.0	1.2	38.2	1.3
	N-L5	64.5	2.5	37.7	3.6
	N-NP55	70.5	1.5	46.1	2.8
High temperature	H-Ref	61.5	0.4	39.4	1.1
	H-L5	62.2	1.6	39.0	3.5
	H-NP55	57.1	1.1	39.9	0.6

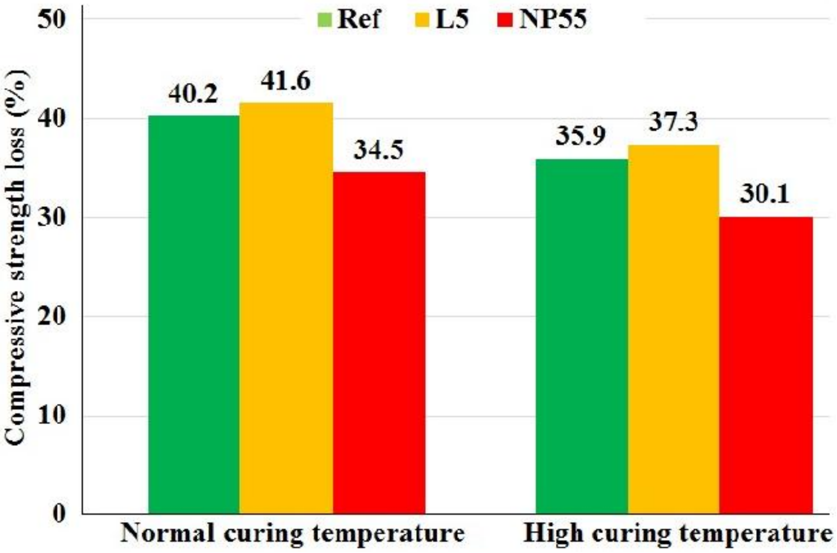

Fig. 5.8. Compressive strength loss of concrete after 22 weeks of immersion in the mixed solution.

5.3.4.4. Neutralization depth

The neutralization depth of concretes after 22 weeks of immersion in the mixed solution is illustrated in Fig. 5.9. It can be seen that the highest neutralization depth was observed in L5 regardless of curing temperature conditions. The lowest neutralization depth was recorded for NP55. It indicates that the addition of Shirasu enhanced the resistance of concrete to the mixed solution attack owing to the pozzolanic reactivity of Shirasu associated with lower $Ca(OH)_2$ content and refinement effect on concrete structure. In contrast, using limestone powder as fine aggregate replacement adversely affected the resistance of concretes because of higher content of $Ca(OH)_2$ and $CaCO_3$ which is vulnerable to the chemical reaction as mentioned in the XRD analysis. Furthermore, the lower neutralization depth was recorded for concretes cured at high temperature in comparison with that of concretes cured at normal temperature because of lower portlandite content and coarser porosity associated with higher absorption capacity of expansion caused by the precipitation of chemical reaction products such as bassanite ($CaSO_4.0.5H_2O$), gypsum ($CaSO_4.2H_2O$), hydrophilite ($CaCl_2$) and epsomite ($MgSO_4.7\ H_2O$).

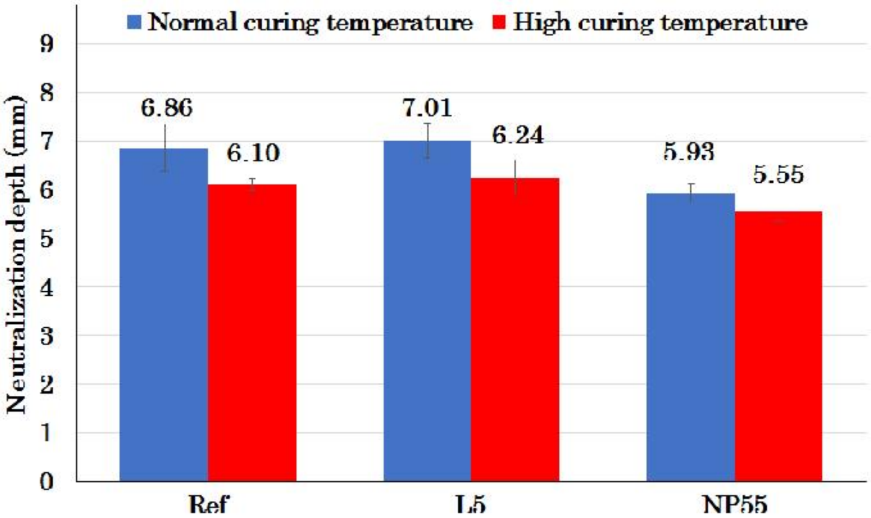

Fig. 5.9. Neutralization depth of concretes after 22 weeks of immersion in the mixed solution

5.3.4.5. Chloride penetration depth

The chloride penetration depth in concrete after 22 weeks of immersion in the mixed solution is presented in Fig. 5.10. It can be seen that concrete using Shirasu as a fine aggregate replacement (NP55) exhibited the lower neutralization depth in comparison with other concretes without Shirasu (Ref and L5). It confirms that Shirasu can enhance the resistance of concrete to the chloride diffusion because of its pozzolanic reactivity. The lower chloride penetration of concrete containing Shirasu could be attributed to pore structure refinement, resulting from the additional hydration products formed by the pozzolanic reaction [30]. The refinement effects might result in the decrease in the connectivity of pores and contribute to impeding the diffusion of ions from external environments into concretes. In addition, chloride penetration depth in concrete containing limestone powder (L5) was lower than that in Ref. It indicates that the addition of limestone powder as a fine aggregate replacement can improve the chloride impermeability of concretes. It is assumed that the filling effect of limestone powder in the voids between aggregates and cement grains could result in the densification of concretes structure.

Furthermore, Fig. 5.10 shows that the chloride penetration depth in concretes cured at a high temperature is higher than that in concretes cured at a normal temperature. It confirms that the elevated curing temperature can result in high chloride permeability of concretes due to higher porosity of concrete structure caused by initial high curing temperature [31,32].

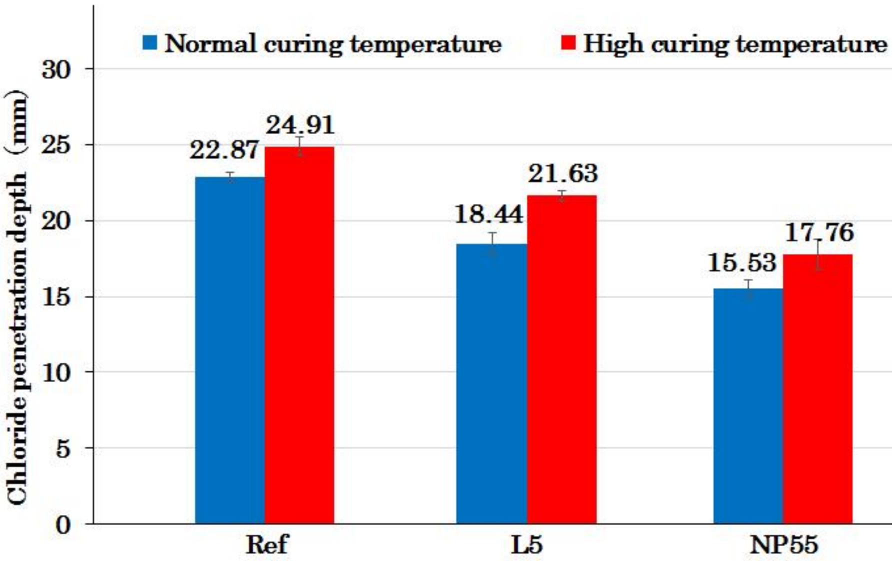

Fig. 5.10. Chloride penetration depth of concretes after 22 weeks of immersion in the mixed solution

5.4. Conclusions

This study analyses effects of initial curing temperature on the strength development and chemical resistance of concretes limestone powder and Shirasu natural pozzolan. The following conclusions can be drawn based on the mechanical and chemical analyses in this work:

- The high initial curing temperature can accelerate the pozzolanic reactivity of Shirasu, leading to an increase the compressive strength of concretes containing Shirasu as a partial fine aggregate replacement at the early age. However, initial high curing temperature tends to reduce the compressive strength of concrete.

- The deterioration of concretes cured at high initial temperature by the attack of a mixed solution containing 3% sulfuric acid and 5% magnesium chloride was less severe than that of concretes cured at normal temperature. On the other hand, high curing temperature can result in higher chloride penetration depth of concretes in comparison with that of concretes cured at normal temperature.

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Chapter 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This study analyses effects of limestone powder and Shirasu natural pozzolan on the strength development and chemical resistance of concrete to the attack of aggressive chemical environment containing H^+, SO_4^{2-}, Mg^{2+}, Cl^- ions which are considered to be the most destructive ions to concrete and can deteriorate its service life and increase the maintenance cost of civil infrastructure. In addition, the effect of initial curing temperature on the strength development and chemical resistance of concretes limestone powder and Shirasu natural pozzolan was also studied. In the study, limestone powder and Shirasu natural pozzolan was used as partial fine aggregate replacement. The proportions of fine aggregate replaced with the limestone powder and Shirasu were 5% and 55% by volume, respectively. 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% $MgCl_2$. Based on the mechanical and chemical analyses, the following conclusions can be drawn in this work:

(1) Effects of limestone powder and Shirasu natural pozzolan

- The addition of Shirasu as a fine aggregate replacement improved the compressive strength of concrete due to its pozzolanic reactivity.
- The effect of limestone powder on strength development was insignificant.
- The addition of Shirasu as a partial fine aggregate replacement improved the resistance of the concrete to an aggressive chemical solution containing 3% H_2SO_4 and 5% $MgCl_2$.
- The concrete using limestone powder as a partial fine aggregate replacement was suffered more severe deterioration of concretes by the aggressive chemical solution. However, the incorporation of the Shirasu compensated for this effect.

(2) Effects of initial curing temperature

- The high initial curing temperature can accelerate the pozzolanic reactivity of Shirasu, leading to an increase the compressive strength of concretes containing Shirasu as a partial fine aggregate replacement at the early age. However, initial high curing temperature tends to reduce the compressive strength of concrete.
- The deterioration of concretes cured at high initial temperature by the attack of a mixed solution containing 3% sulfuric acid and 5% magnesium chloride was less severe than that of concretes cured at normal temperature. On the other hand, high curing temperature can result in higher chloride penetration depth of concretes in comparison with that of concretes cured at normal temperature.

(3) The deterioration mechanism of concretes caused by the attack of aggressive environment containing 3% sulfuric acid and 5% magnesium chloride

- 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 ($CaSO_4.0.5\ H_2O$), epsomite ($MgSO_4.7\ H_2O$), and hydrophilite ($CaCl_2$), silica gel (SiO_2). Herein, 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 of the concrete structure.

6.2. Recommendations for future study

The present study investigated the effects of limestone powder and Shirasu natural pozzolan on the strength development and chemical resistance of concrete cured at the different initial temperatures. Some recommendations for future work can be made in detail as follows:

- In the study, only the content of limestone powder of 5% and Shirasu of 55% as partial fine aggregate replacements were designated based on those reported in some previous studies. It is necessary to extend for various amounts of content of limestone powder and Shirasu should be tested to determine at what point the addition of limestone and Shirasu stop being effective.

- In the study, a limited test for investigating the effect of limestone powder and Shirasu were carried out. It is necessary to extend for other tests, such as elastic modulus, tensile strength, water permeability, carbonation, alkali-silica reaction, etc.
- Because of the limited time, an accelerated test with the use of a mixed solution containing 3% sulfuric acid and 5% magnesium chloride was used for simulating the attack of an aggressive chemical environment. Therefore, other test solutions with various concentrations of sulfuric acid and magnesium chloride should be done in order to simulate various conditions in the site. In addition, other tests using the original environment, such as water in acid sulfate soil areas, should be conducted in further study to simulate the real condition.
- Regarding investigation of temperature on the performance of concrete, a high curing temperature history of 60°C for 8 hours was adopted for specimens in the present study. Other temperatures curing regimes should be applied to obtain the optimum curing temperature for the performance of concretes contaning limestone powder and Shirasu.
- In addition, the other curing conditions that can affect the mechanical properties and durability of concrete should be adopted in the future works, such as steam curing or drying condition without sealed aluminum tape in the air at ambient temperature.

Appendix: Publications arising from this research

List of papers were published or in the process of publishing from this research:

A. Academic Journals

1) Van Toan Pham, Phalkong Meng, Phuong Trinh Bui, Yuko Ogawa, Kenji Kawai, Effects of shirasu natural pozzolan and limestone powder on the strength and aggressive chemical resistance of concrete, Construction and Building Materials, Vol. 239 117679 online (2020). DOI: 10.1016/j.conbuildmat.2019.117679.

2) Toan V. Pham, Meng Phalkong, Yuko Ogawa, Kenji Kawai, Deterioration of concretes containing Shirasu natural pozzolan and limestone powder exposed to aggressive chemical environment, Proceeding of the Japan Concrete Institute. Vol. 41, No.1, (2019), pp. 647-652.

3) V.T. Pham, M. Phalkong, Y. Ogawa, K. Kawai, Effects of Shirasu Volcanic Ash and Limestone Powder on Chemical Resistance of Concrete, Proceeding of the 8th International Conference of Asian Concrete Federation, Vol. 1 (2018), pp. 483-493.

B. Presentations at International Conferences

1) V.T. Pham, M. Phalkong, Y. Ogawa, K. Kawai, Effects of shirasu volcanic ash and limestone powder on chemical resistance of concrete, The 8th International Conference of Asian Concrete Federation – ACF 2018, Fuzhou, China (2018).

2) Toan V. Pham, Meng Phalkong, Yuko Ogawa, Kenji Kawai, Deterioration of concrete containing Shirasu natural pozzolan and limestone powder exposed to aggressive chemical environment, Japan Concrete Institute - JCI Annual Convention 2019, Sapporo, Japan (2019).