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The strength development and chloride permeability of concrete containing natural pozzolan and limestone powder at different curing temperatures

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ABSTRACT

This study investigated the strength development and chloride permeability of concretes by considering not only the effects of limestone powder and natural pozzolan but also the initial curing temperature. The study examined the mechanical and chemical changes in the concretes cured at different initial curing temperatures, including 20°C and 60°C. The results revealed that the compressive strength of concrete containing natural pozzolan was higher than that of the concrete without natural pozzolan after 28-day curing at 20°C, namely normal temperature. 60°C, namely high curing temperature, was responsible for increases in the compressive strength of concretes at early ages and reductions at later ages in comparison with that of concretes cured at normal curing temperature. The effect of limestone powder on concrete strength was insignificant at both curing temperatures. Furthermore, using natural pozzolan and limestone powder as a fine aggregate replacement improved the chloride impermeability of concretes.

1. Introduction

Concrete has been faced with requirements to improve performance, reduce energy consumption, and diversify raw materials supply. Although the efficiency of cement has been increasingly improved, the energy consumption and CO_2 emissions in cement manufacturing are still concerns. The process has resulted in a harmful impact on the environment. Therefore, the demand to utilize other cementitious materials in the construction industry has been urgent. As a result, many investigations on the usage of mineral additions such as limestone filler, blast furnace slag, fly ash, silica fume, and natural pozzolan have been carried out [1], [2], [3]. Using limestone in concrete, including as a constituent of cement and aggregate, is common all over the world because of its technical and economic advantages. The Canadian standard CAN/CSA-A3000-08 [4] allows the addition of limestone in Portland cement with a limestone content of total binders below 15%. It is reported that the incorporation of up to 10% limestone powder

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in blended cement affected the hydration process, including an increase in the amount of bound water and compressive strength [1].

In addition, natural pozzolan has been widely used to produce more environmentally sustainable concretes due to technical benefits such as reduction in energy consumption, improvement of durability, ultimate strength of concrete, and decrease in CO_2 emission compared with ordinary Portland cement concrete [2], [3]. Regarding the compressive strength, Behfarnia et al. [5] reported that the replacement of cement by 15% metakaolin and 10% zeolite resulted in higher compressive strength compared to normal self-consolidating concrete using only ordinary Portland cement.

Furthermore, curing temperature has a large influence on the microstructure, hydration process, and pozzolanic reaction of blended cement paste, resulting in the mechanical properties and durability of concrete [6], [7]. The cement hydration process was accelerated at a high curing temperature at the early stage. However, at the later age, the situation was reversed because the rapid hydration did not allow for sufficient time for the hydration products to diffuse within the pore structure and arrange evenly, leading to an inhomogeneity in microstructure, followed by coarser porosity and a reduction in ultimate strength. This behavior has been called the crossover effect [8].

For the aforementioned reasons, the effects of limestone powder and natural pozzolan used as fine aggregate replacements in concrete were investigated in this study concerning the compressive strength development and the chloride permeability of concrete. In addition, the influence of curing temperature on the mechanical properties and the durability of concrete was investigated to determine the most effective curing conditions for concrete, considering technical and economic factors.

2. Methods and materials

2.1. Materials

The experimental study was carried out on concrete with limestone powder (L), and natural pozzolan (N) used as the fine aggregate replacement. The cementitious material used in this study was ordinary Portland cement (C) with a fineness of 3290 cm^2/g. The chemical and mineralogical compositions of different compounds of cement, limestone powder and natural pozzolan used in this study are presented in Table 1.

Crushed quartz porphyry was used as the conventional fine and coarse aggregates. The density of limestone powder was 2.7 g/cm^3. Also, the densities of fine aggregate, coarse aggregate, and natural pozzolan in saturated surface-dry conditions were 2.6 g/cm^3, 2.6 g/cm^3, and 2.1 g/cm^3, respectively. The water absorption of fine aggregate, coarse aggregate, and natural pozzolan was 1.04%, 0.6%, and 9.27%, respectively. In addition, the pozzolanic reactivity of natural pozzolan was determined by using the API method [9] with an API value of 14.4%. which indicates that natural pozzolan possesses pozzolanic reactivity and is lower than that of commercial low-calcium fly ash with API value of 25%~85%.

2.2. Mixture proportion

A constant ratio of water-to-cement (W/C) of 0.40 and a cement content of 425 kg/m^3 were used for all concrete mixtures. The replacement ratios of fine aggregate by limestone powder and natural pozzolan were 5% and 55% by volume, respectively. Concrete mixtures were designated the following labels: Ref, L5, and N55, as shown in Table 2. Reference concrete (Ref) is defined as concrete with 0% replacement by limestone powder and natural pozzolan. Superplasticizer (MasterGlenium SP8HVM Polycarboxylic ether compound) (BASF Japan Ltd., Japan) was used to obtain the designed value of slump of 10 ± 1 cm without increasing the water content. The particle size distribution of fine aggregate of concrete mixtures is also presented in Figure 1.

Table 1. Chemical composition of materials.

Composition (%)	OPC (C)	Fine aggregate		
		Limestone (L)	Natural pozzolan (NP)	Crushed quartz porphyry (S)
SiO_2	20.3	0.2	73.6	75.6
Al_2O_3	4.9	-	14.7	13.2
Fe_2O_3	2.9	0.06	2.6	2.1
CaO	65.0	55.7	2.0	1.1
MgO	1.2	-	0.3	0.9
SO_3	1.9	0.2	0.07	-
Cl^-	0.01	-	0.06	-
LOI	2.4	43.9	2.4	0.6

Table 2. Mixture proportion of concrete.

Mixture	W/C	Unit content (kg/m^3)						Slump (cm)
		C	W	Fine aggregate			Crushed quartz porphyry	
				L	NP	S		
Ref	0.40	425	170	0	0	758	1005	9.5
L5	0.40	425	170	39	0	720	1005	9.5
N55	0.40	425	170	0.00	337	341	1005	9.5

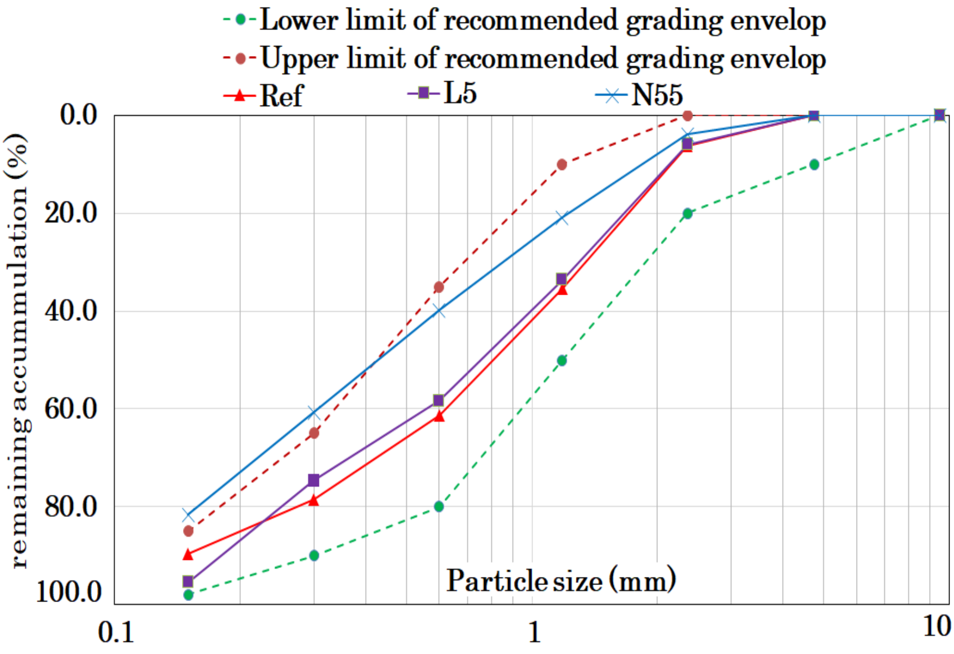

Figure 1. The particle size distribution of fine aggregate.

2.3.Specimen preparation and curing

Cylindrical specimens of 100 mm in diameter and 200 mm in height were produced. After casting, specimens of each concrete mixture were separated into two groups: one was a normal curing temperature condition in which specimens were cured in a sealed condition by aluminum tape at 20°C until the designated test age (i.e., until 3, 28, and 91 days for the compressive strength measurements); the other was a high curing temperature condition in which specimens were cured at a high temperature history of 60°C for 8 hours followed by 20°C with a sealed condition by aluminum adhesion tape until the designated test ages. The schematic of the heat treatment regime, which followed the curing temperature history of Corominas et al. [10], is shown in Figure 2.

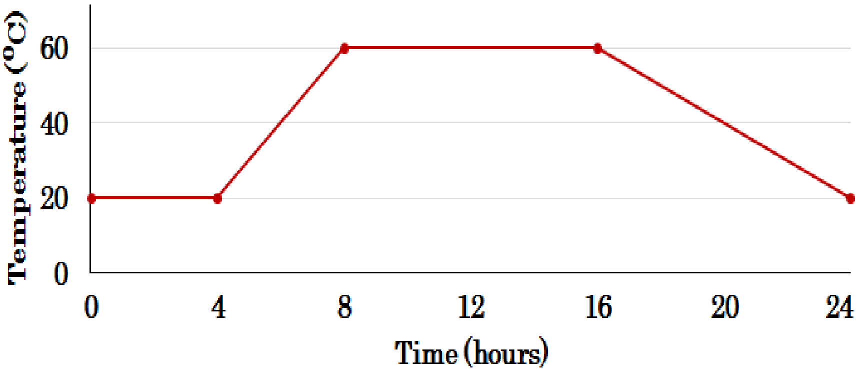

Figure 2. Schematic representation of the heat treatment procedure.

Figure 3. TG-DTA method for determining the $Ca(OH)_2$ content in concrete.

Figure 4. Test method for compressive strength of concretes .

2.4. Experimental methods

2.4.1. Compressive strength

Three cylindrical specimens of 100 mm in diameter and 200 mm in height for each concrete mixture were tested to determine the compressive strength at the ages of 3, 28, and 91 days after casting according to JIS A 1108-2006 [11] (Japanese Industrial Standard: Method of test for compressive strength of concrete). The test method of compressive strength is shown in Figure 4.

2.4.2. $Ca(OH)_2$ content

The $Ca(OH)_2$ content in pastes of concrete specimens was measured at the age of 3, 28, and 91 days after casting. The sample was collected from the center part of the concrete after the compressive strength test. After soaking in acetone for over 24 hours to stop further hydration reaction immediately after collection, the samples were dried in a vacuum desiccator for 24 hours and crushed into fine powder with the maximum particle size of 150 µm by using a milling machine to obtain the homogenous powder blends.

In this study, due to the addition of limestone powder as fine aggregate, the determination of cement pastes and aggregate content was carried out by the Sodium Gluconate dissolution method [12]. This chemical test was performed such that approximately 0.5 g of concrete powder was added to 200 mL of 15% sodium gluconate solution. The solution was mixed using a magnetic stirrer at 300 rpm (rounds per minute) and at a control temperature of 20°C for 30 min. The filter paper was also prepared by placing it in a heating oven at 105°C followed by cooling down it in a desiccator for 30 min before measuring the weight of the filter paper (m_f). After stirring, the solution was filtered through filter paper to obtain a residue. This residue was dried at 105°C for 12 hours to eliminate free water, followed by cooling in the desiccator for 30 min. After that, the mass of residue after drying was measured.

The $Ca(OH)_2$ content in the paste from concrete powder with a size of less than 150 µm was determined by TG-DTA. The concrete powder was heated from room temperature to 100 °C at 20 °C/min, kept at 100°C for 30 min to remove free water, and then heated to 1000°C at 20°C/min. The $Ca(OH)_2$ content was calculated by combining the results of the chemical test and TG-DTA by following the formula:

$$CH = \frac{CH_1}{C} \times 100 \qquad (1)$$

Where,

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

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

C: The cement paste content in a sample calculated from the chemical test result [12].

$$C(\%) = \frac{m_s + m_f - m_r}{m_s} \times 100 \qquad (2)$$

Where,

m_s: The mass of the concrete powder sample;

m_f: The mass of filter paper;

m_r: The mass of residue after drying.

The test method of $Ca(OH)_2$ content by TG-DTA is shown in Figure 3.

2.4.3. Effective chloride diffusion coefficient measurement

In this study, the steady-state migration test [13], [14] was adopted to measure the diffusion coefficient of chloride ion. After 56 days of curing, concrete specimens were cut into slices 30 mm thick for the test. After storing the specimen at 20°C and 60 ± 5% RH (relative humidity) for four hours, the specimens were coated by epoxy resin, except for 2 bottom surfaces. The test method of the migration test is shown in Figure 5 [13], [14]. Effective chloride diffusion coefficients were determined on three concrete discs (∅100 x H30 mm) per mixture proportion. This test accelerated chloride diffusion by an electrical potential of 12 V, but the measured potential dropped to approximately 10 V and was used in the diffusion coefficient calculation. The concentration of chloride used was 0.564 M. The test was carried out at 20°C. The diffusion coefficients were calculated from the chloride flux in the cathodic cell in the steady state. The chloride concentration was measured by ionic chromatography. The flux of chloride ions in the steady state is calculated as the following equation:

$$J_{Cl} = \frac{V}{A}\frac{\Delta C_{Cl}}{\Delta t} \qquad (3)$$

Where,

J_{Cl}: Flux of chloride ions in steady state (mol/m^{2}s);

V: Volume of solution in the anode compartment (m^3);

A: Cross section area of concrete sample (m^2);

$\Delta C_{Cl}/\Delta t$: The increase in concentration of chloride ions in the anode (mol/m^3/s).

Giving $\Delta C_{Cl}/\Delta t$ as the slope. The effective chloride diffusion coefficient is calculated using the following equation:

$$D_e = \frac{J_{Cl} RTL}{|z|EFC_{Cl}} \qquad (4)$$

Where,

D_e: Effective diffusion coefficient (m^2/s);

R: Gas constant (8.3144 J/molK);

T: Absolute temperature (K);

Z: Charge of chloride ion (=-1);

F: Faraday constant (=96480 J/(V mol));

C_{Cl}: Average measured chloride ion concentration in the cathode (mol/m^3);

E: Electrical potential difference between specimen surfaces (V);

L: Length of specimen (m).

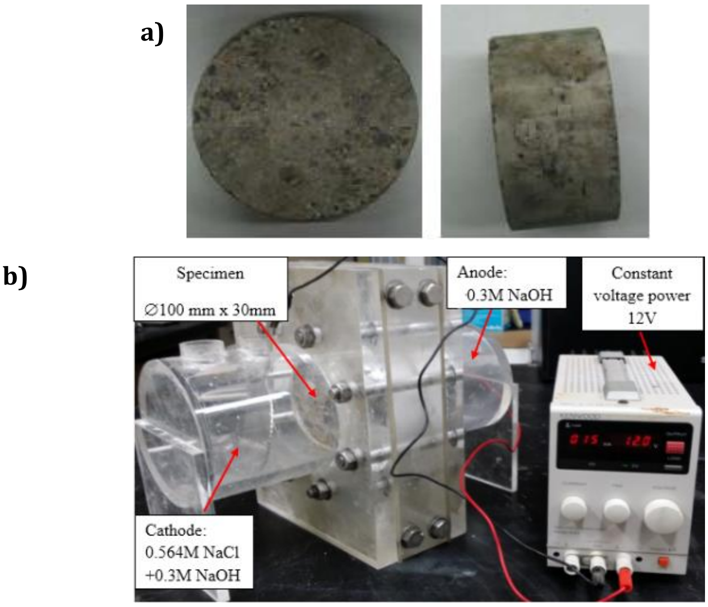

Figure 5. The specimen (a) and test method for effective diffusion coefficient of chloride ions in concrete by migration (b) referring to the Truc et al. method and JSCE-G571 standard.

3. Results and discussion

3.1. Calcium hydroxide $Ca(OH)_2$ content

The content of $Ca(OH)_2$ in the concrete cured for 3, 28, and 91 days is measured according to the data of TG-DTA and chemical tests to determine the cement content in concrete samples. Table 3 and Figure 6 show the $Ca(OH)_2$ content of the concrete sample at both normal and high curing temperature conditions. It can be seen that at normal curing temperature, the $Ca(OH)_2$ contents in concretes substantially reduced with the addition of natural pozzolan at the age of 28 and 91 days in comparison with $Ca(OH)_2$ content in concretes without natural pozzolan, whereas the $Ca(OH)_2$ content in N55 at normal curing temperature was approximately similar to that in Ref at the age of three days. The reduction in $Ca(OH)_2$ content can be attributed to the pozzolanic reactivity of natural pozzolan, which consumed $Ca(OH)_2$. It is dedicated to the fact that at normal curing temperature, the pozzolanic reactivity of natural pozzolan was not promoted at an early age of three days. The effect of natural pozzolan on concrete properties only showed at later ages (after 28 days). Furthermore, the $Ca(OH)_2$ content of concretes containing natural pozzolan decreased with the increase in curing temperature at the early age. At the age of 3 days, the $Ca(OH)_2$ content in N55 was significantly lower than that in Ref at a high curing temperature condition. It can be inferred that elevated temperature can excite the pozzolanic reactivity of natural pozzolan, which accelerates the consumption of $Ca(OH)_2$. In addition, using limestone as a fine aggregate replacement seems to have little effect on the $Ca(OH)_2$ content in all concretes regardless of the curing temperature. It was a reason that the $Ca(OH)_2$ content of L5 is almost identical to that of Ref concrete cured at both curing temperatures at different curing ages.

Table 3. $Ca(OH)_2$ content in concrete (%).

Mixture	3 days	28 days	91 days
Ref	11.91	14.88	16.18
L5	11.83	14.79	16.37
N55	11.90	13.07	13.91
H-Ref	12.28	13.29	15.25
H-L5	12.49	13.37	14.83
H-N55	11.32	11.93	12.60

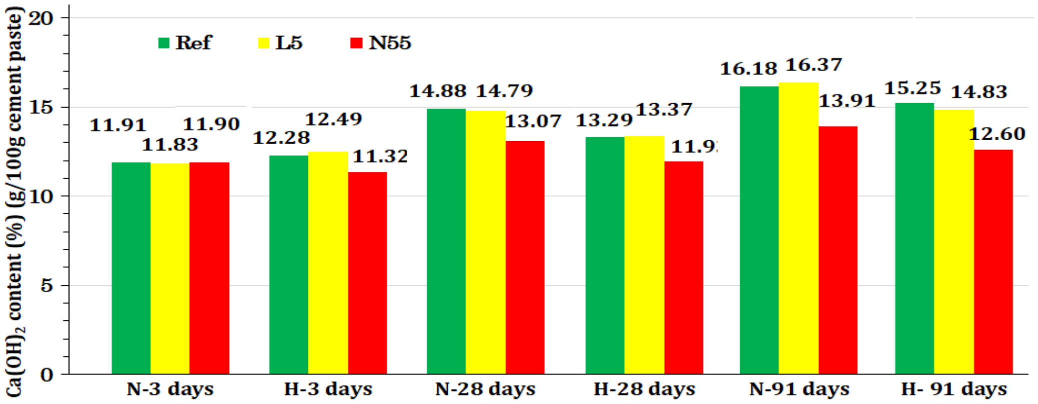

Figure 6. Content of calcium hydroxide in cement pastes of concretes cured at different temperatures: N- normal curing temperature; H- high curing temperature.

3.2. Compressive strength

The compressive strength of concrete specimens at different curing ages is illustrated in Table 4 and Figure 7**.** It can be observed that at normal curing conditions, at the age of three days, the compressive strength of concrete containing natural pozzolan-N55-is almost the same as those of Ref and L5. However, at a later age, the compressive strength of N55 is significantly higher than that of concrete without natural pozzolan (L5 and Ref) after 28 and 91 days of normal curing temperature conditions. Considering the results of the $Ca(OH)_2$ content, it can be said that the pozzolanic reaction between natural pozzolan and calcium hydroxide $Ca(OH)_2$ produced additional hydration products, namely calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), refined the pore structure [7], and led to the strength development of concretes. Furthermore, Figure 7 also shows that under high curing temperature conditions, the compressive strength of concrete containing natural pozzolan moderately exceeds that of concrete without natural pozzolan regardless of curing age. It indicates that initial high curing temperature can accelerate the pozzolanic reaction, leading to the promotion of the compressive strength of concrete containing natural pozzolan.

Table 4. Compressive strength of concrete (MPa).

Mixture	**Time-curing**			**Designed compressive strength at 28 days (MPa)**
	3 days	**28 days**	**91 days**	
Ref	38.19	50.89	58.5	40
L5	38.24	50.72	61.7	40
N55	37.26	60.40	66.3	40
H-Ref	39.75	47.76	53.0	40
H-L5	40.04	46.41	55.1	40
H-N55	42.04	48.67	57.9	40

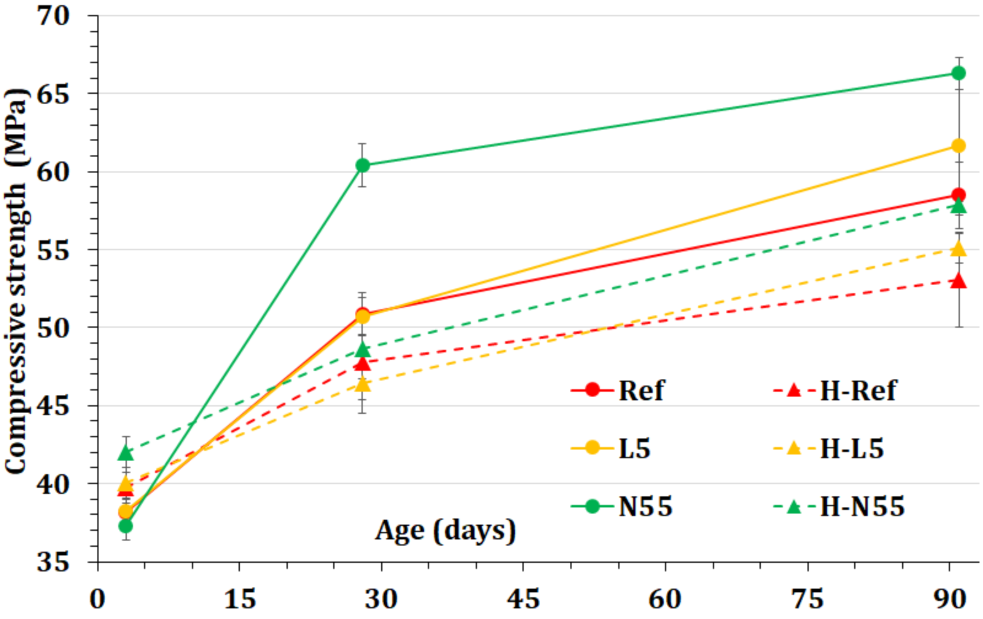

Figure 7. Compressive strength of concretes at the ages of 3, 28, and 91 days cured at different temperatures: N- normal curing temperature; H-high curing temperature.

At the time of casting specimens, natural pozzolan demonstrated a high water absorption capacity of 9.27% and a measured moisture content of 8.08%. Presumably, a concrete mixture with natural pozzolan performed as an internal curing agent, which can provide additional moisture for hydration and a pozzolanic reaction. Internal curing effect can contribute to strength development of concretes at the later ages [15]. In the case of L5 concrete, the effect of limestone powder on the compressive strength of concrete was not prominent. The strength of L5 was almost the same as that of Ref regardless of curing ages at both curing temperatures. In addition, it can be seen that the early-age compressive strength of concretes cured at high curing temperature was higher than that of concretes cured at normal curing temperature. On the other hand, the later-age compressive strength of all concrete mixtures at high curing temperature condition was less than that of concrete at normal curing conditions after 28 and 91 days of curing. This result agreed with the previous studies [7], [8]. It was reported that the compressive strength of concretes cured at elevated curing temperature is higher at early an age of curing but lower at a later age in comparison with that of concretes cured at normal curing temperature. The reason for this phenomenon is that at a high temperature, the rapid hydration did not allow for sufficient time for the hydration products to diffuse within the pore structure and arrange evenly, leading to an inhomogeneity in microstructure, followed by coarser porosity and a reduction in ultimate strength. This behavior had been so-called the crossover effect [8].

3.3. Chloride diffusion coefficient

Figure 8 and 9 show the total increase of chloride concentration in the anode solution over time and the chloride diffusion coefficient of mixture proportions, respectively. It is indicated that the lowest rate of chloride diffusion was recorded for concretes containing natural pozzolan (N55) regardless of curing temperature condition, followed by the rate of chloride diffusion of L5. Ref concrete containing only OPC showed the highest rate of chloride diffusion. Obviously, the addition of natural pozzolan improved the resistance of concrete to chloride immigration because the pozzolanic reaction led to the formation of secondary cementitious material, which contributed to the refinement of the pore structure and the reduction of the interconnection of pores. This result also agreed with the report of Takewaka et al. [15] on the resistance of concrete using natural pozzolan as fine aggregate to the chloride-induced deterioration during three years of immersion in the tidal sea area.

In addition, the effective chloride diffusion coefficients of concretes at normal curing were lower than those of concretes cured at high curing temperatures. Presumably, higher porosity of concretes cured at high curing temperature [7] resulted in a higher chloride penetration rate than the chloride penetration rate of concretes cured at normal curing temperature. Detwiler et al. [16] also reported that elevated curing temperatures result in a coarser pore structure and a corresponding decrease in the resistance to chloride ion diffusion.

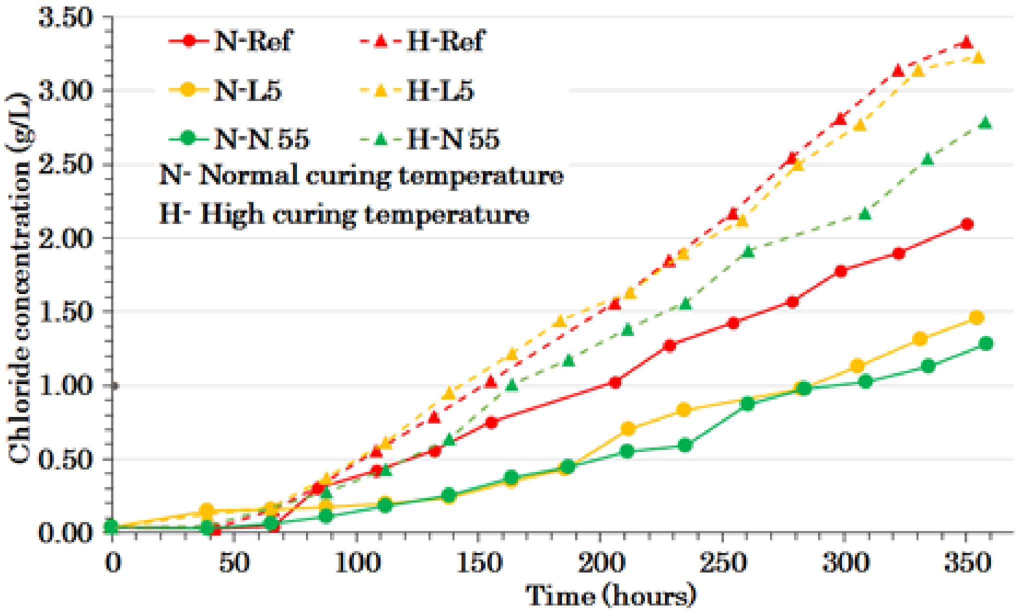

Figure 8. Cumulative increase of chloride concentration in anode sections with the concretes cured at different temperatures: N- normal curing temperature; H- high curing temperature.

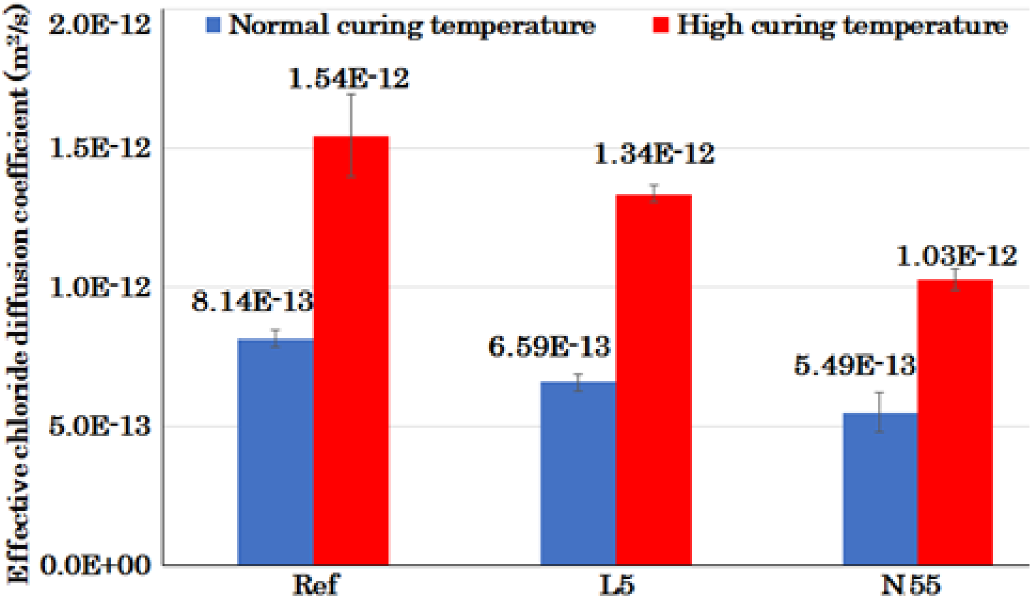

Figure 9. Effective chloride diffusion coefficient of concretes cured at different temperatures.

4. Conclusions

The influence of curing temperature on the mechanical properties and the durability of concrete was studied. In addition, the effects of limestone powder and natural pozzolan used as fine aggregate replacements in concrete were also investigated concerning the compressive strength development and the chloride permeability of concrete. Based on the experimental results, the conclusions could be summarized as follows:

At normal curing temperatures, using natural pozzolan as a fine aggregate replacement can improve the strength development of concretes after 28 days of curing.

Concretes containing natural pozzolan also exhibited higher resistance to chloride ion penetration than reference concrete.

The effect of limestone powder as a fine aggregate replacement on the compressive strength development of concrete was not significant at both normal and high curing temperatures.

High curing temperature could promote the compressive strength of concretes at early ages. However, the compressive strength of concrete cured at high curing temperature decreased at a later age compared to that of concrete cured at normal curing temperature. High curing temperatures reduced the resistance to chloride ion ingress.

Declaration of competing interest and dedication to copyright

The author declares the absence of any potential conflicts of interest from this study and affirms that the paper has not been previously published.

Data available

Data will be provided upon request.

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