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Application of thermoporometry for evaluation of properties of hardened cement paste

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HIGHLIGHTS

- Thermoporometry (TPM) was applied to the evaluation of hardened cement paste properties.
- Good correlation was seen in pore volume measured by TPM and properties.
- It is possible to evaluate properties of hardened cement paste by TPM using LT-DSC.

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ABSTRACT

Mercury intrusion porosimetry (MIP) has been widely used for the evaluation of the pore structure of hardened cement paste. However, treatment with mercury is dangerous and causes environmental damage. Therefore, we investigated the pore structure of hardened cement paste by thermoporometry (TPM) using low-temperature differential scanning calorimetry (LT-DSC) measurements as an alternative to MIP in this study. The compressive strength, ultrasonic pulse velocity, and electrical conductivity were measured as the properties of hardened cement paste. Good correlation was demonstrated between the pore volume measured by TPM and these properties. It was shown that it is possible to evaluate the properties of hardened cement paste by TPM using LT-DSC.

1. Introduction

When evaluating the durability of a concrete structure, it is necessary to know its exact mechanical and transport properties, such as diffusion and permeability. These properties are greatly influenced by its pore structure. Therefore, it is very important to precisely measure the pore structure of concrete structures. Mercury intrusion porosimetry (MIP) has been widely used for the evaluation of the pore structure of hardened cement paste [1]. However, it has been demonstrated that MIP cannot measure the true pore structure because of the ink bottle effect [2]. In addition, it is necessary to dry a sample for MIP measurements. Moreover, treatment with mercury is dangerous and causes environmental damage. To overcome such problems, thermoporometry (TPM) using low-temperature differential scanning calorimetry (LT-DSC) has been suggested to measure the pore structure of cementitious materials [1]. Some studies on LT-DSC have reported the freeze temperature of pore water and relations of the pore radius [3–6]. The TPM was used to investigate the behavior of freeze–thawing action and the transport properties of cementitious materials [7,8]. There are some discussions about measurement technique and analysis of TPM [6,9], a further study is necessary. Conversely, there have been numerous studies comparing the pore volume measured by MIP and the properties of hardened cement paste [10–14]. However, there have been no studies comparing the total number of pores measured by TPM and the properties of hardened cement paste. Therefore, the application of TPM using LT-DSC was investigated as an alternative technique for MIP. In this study, the relationships between the pore volume and the compressive strength, ultrasonic pulse velocity, and electrical conductivity were given particular focus.

2. Experimental procedure

2.1. Materials

In this study, ordinary Portland cement (OPC, density: 3.17 g/cm^3, specific surface area: 3340 cm^2/g) and ground granulated blast furnace slag (density: 2.91 g/cm^3, specific surface area: 3960 cm^2/g) were used, as shown in Tables 1 and 2. The water-to-cement ratio of the OPC samples were 0.3, 0.5, and

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Table 1
Chemical composition of cement (mass%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
21.56	4.68	2.98	65.63	1.30	1.90	0.33	0.39

Table 2
Chemical composition of slag (mass%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
34.03	14.36	0.83	43.28	6.51	0.18	0.31

0.7. The water-to-binder ratio of the sample with added slag was 0.5, and the replacement ratio of the slag was 0.5 and 0.7. (These samples are labeled "0.5–0.5" and "0.5–0.7," respectively, in the figures in this study.) The paste was mixed repeatedly to avoid bleeding and placed a mold. After 24 h, the specimens were demolded and cured in saturated lime water at 20 °C for 28 and 91 days.

2.2. Measurement

2.2.1. Thermoporometry (TPM)

Pieces of the hardened cement paste (HCP) samples weighing 28 mg were cut from the cured test piece with saturated condition and measured by LT-DSC to obtain the quantity of heat of the exothermic peak during the freezing process. Each HCP sample was placed in a sealed aluminum pan to avoid water evaporation during the measurement. The measurement conditions were as follows: the starting temperature was 10 °C, the temperature range during cooling was −60 to 10 °C, and the cooling rate was 0.5 °C/min. As a reference, alumina powder was measured simultaneously. The pore radius was determined by [3,5]

$$R_{freeze} = -\frac{64.67}{\Delta T} + 0.57 \quad (1)$$

$$R_{melt} = -\frac{32.33}{\Delta T} + 0.68, \quad (2)$$

where R_{freeze}: pore radius during the freezing process (nm), R_{melt}: pore radius during melting process (nm), ΔT: temperature difference between 273 (K) and measured temperature (K). It has been reported that the composition of the pore solution has little influence on the pore radius [6]. Therefore, the equations for pure water were used in this study. The pore volume at an arbitrary pore radius was calculated from the measured heat release, density of ice, and enthalpy change as [4]

$$\Delta H \text{ (freezing)} = 332.4 \quad (3)$$

$$\Delta H \text{ (melting)} = 333.8 + 1.797\Delta T, \quad (4)$$

where ΔH: enthalpy change of H_2O at the liquid–solid phase transition (J/g).

2.2.2. Compressive strength

The uniaxial compressive strength of each sample was determined using a cylinder specimen with a diameter of 50 mm and a height of 100 mm.

2.2.3. Ultrasonic pulse velocity

The ultrasonic pulse velocity of each sample was measured using a cylinder specimen with a diameter of 50 mm and a height of 100 mm, as with the compressive strength measurement. The elastic wave velocity of the longitudinal wave (P wave) in each specimen was measured. The ultrasonic pulse velocity of each specimen was determined from the transmission time and the length of the specimen.

2.2.4. AC impedance measurement

The size of the specimens used for the electrical conductivity measurements was 40 mm × 40 mm × 40 mm, and stainless electrodes (40 mm × 30 mm × 0.3 mm) were placed 30 mm apart on the specimen. The effective area of the electrodes is 30 mm × 30 mm, and the AC impedance of the specimens was measured in the range of 4 Hz to 5 MHz with an impedance analyzer (HIOKI IM3570). After the measurements, a Nyquist plot was established from the acquired data, and the bulk resistivity σ was determined from the point where the plotted electrode resistivity (straight line) and a circle cross. The conductivity σ_0 of the pore solution was calculated based on previous studies from the degree of hydration and the chemical composition of the cement [15,16]. The normalized conductivity σ/σ_0 was determined from the bulk resistivity σ and the conductivity σ_0 of the pore solution.

2.2.5. MIP

MIP was used to measure the pore size distribution for pores with diameters ranging from 3 nm to 400 μm (curing ages: 28, 91 days). The specimens for this measurement were dried using the freeze-dry method.

2.2.6. Loss of ignition

The loss of ignition *Wn* from 105 to 950 °C was measured to determine the degree of hydration in the specimens. The non-evaporable water content of the fully hydrated cement paste was 0.23 here.

2.2.7. Porosity

The porosity was determined from the density of the specimen and the difference between the weight of the saturated sample and that of the dried sample at 105 °C.

3. Results and discussion

3.1. Properties of hardened cement paste

The properties of the hardened cement pastes are shown in Figs. 1–3. The compressive strength and ultrasonic pulse velocity of the specimen increased with curing age, as shown in Figs. 1 and 2, respectively. The increase in the compressive strength for the specimen mixed with slag was higher than that of the OPC specimen. The electrical conductivity decreased with curing age, as shown in Fig. 3. The decrease in the electrical conductivity for the specimen mixed with slag was high, and it was expected that the ion migration changed significantly.

3.2. Pore volume

The cumulative pore volumes of hardened and blended cement pastes measured by TPM during the freezing process are shown in

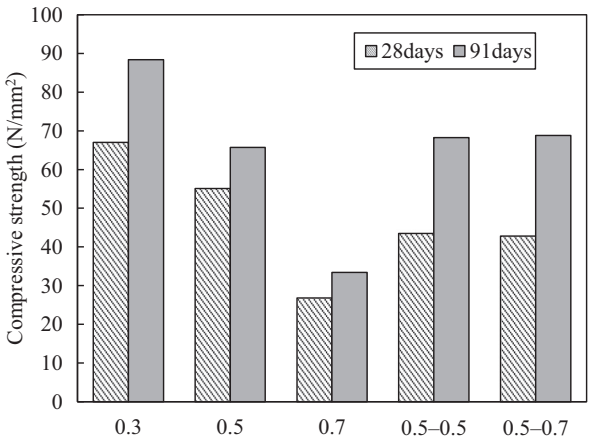

Fig. 1. Compressive strength of hardened cement pastes.

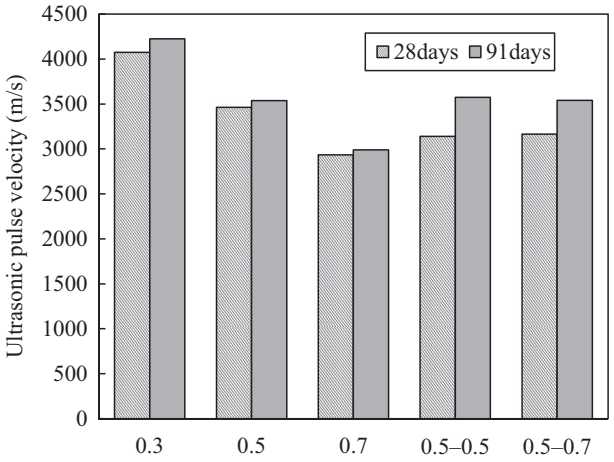

Fig. 2. Ultrasonic pulse velocity of hardened cement pastes.