Analysis of pore structure using DSC for porous materials

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1. Introduction
Mercury intrusion porosimetry (MIP) is widely used as an effective technique for characterization of pore structure around several nm to 20μm and this method is used for the measurement of cement and concrete. But this method is harmful using mercury. In the future, the chance of analytical method using harmful substance is low and new measurement for characterization of pore structure is needed. Also, MIP has a possibility that high pressures may be crushed the week hardening body e.g. deteriorated concrete.

Recently, thermoporometry is watched as new analytical approach for characterizing pore structure. Depression of melting or freezing point of liquid confined in a pore is different according to pore size, and pore size distribution of porous material is obtained by measurement of differential scanning calorimetry (DSC). But, retrospective report use silica gel and porous glass that have even pore structure. Cement and concrete have uneven pore structure and a research that applies to cement and concrete is few.

This study discusses the analysis of measurement condition and pore structure for porous ceramics by thermoporometry using DSC compare with pore structure using mercury intrusion porosimetry.

2. Thermoporometry
Thermoporometry (TP) is a calorimetric method that determines pore size based on the melting or crystallization point depression of a liquid confined in a pore. Thermodynamic relationship between pore size \( r_p \) and melting or freezing point depression \( \Delta T \) is obtained following equation from the Laplace and Gibbs-Duhem equations.

\[
r_p = \frac{2\gamma^{s,l}v_mT_0\cos\theta}{\Delta H_m\Delta T}
\]

\( \gamma^{s,l} \): surface tension between solid and liquid
\( \theta \): contact angle
\( T_0 \): triple point of liquid
\( v_m \): molar volume of liquid
\( \Delta H_m \): molar heat between solid and liquid

Ihiskiriyama et al suggested empirical formula using water and silica gels as follows.

\[
r_p = \frac{3330}{\Delta T} + 0.32 + \delta_m, \quad 0.5 \text{nm} < \delta_m < 2.2 \text{nm} \quad \text{(melting)}
\]

\[
r_p = \frac{5636}{\Delta T} + 0.90 + \delta_f, \quad 0.5 \text{nm} < \delta_f < 2.8 \text{nm} \quad \text{(freezing)}
\]

\( \delta \): thickness of nonfreezable liquid

3. Experiment
Porous silica Q-15, and Q-50 (Fuji Silysia Chemical ltd.) was used. average pore radius of Q-15 is 8.2nm and Q-50 is 23.5nm. Samples were dried at 105°C for 24 hours and immersed in water for 3hours. After immersion, water of adhesion is wiped off and samples were encapsulated in sample pan. The mass change of samples before or after immersion is measured.

Heat curve on heating process around -30°C to 5°C is measured by heat flow type DSC, and pore size distribution is calculated by using eq(2). Also, measurement of freezing process is excluded because repeatability of measured freezing point is not obtained by supercooling phenomenon of water. Obtained pore size distribution is compared with the result of measurement by MIP.

4. Results and Discussion
Pore size distributions of Q-15 by MIP and TP that rate of temperature changes are different are shown in Fig.1. From the result of MIP, Q-15 has small range distribution and even pore structure. For TP, pore size is around 2nm smaller than MIP but distributions are small and good correspondent to MIP when the rate of temperature change are 0.05 or 0.2°C/min. On the other hand, the width of distribution extends to the large diameter side when rate of temperature change increases form the result of 0.5 and 1.0°C/min. It is because that a temperature of furnace in DSC increases greatly before ice in pore melts enough. It is necessary to consider an influence of melt rate and rate of temperature change set under 0.2°C/min. but the case of measurement less than 0.05°C/min, detected heat amount is very small and noise grows larger. It is thought that a rate of temperature change is appropriate...
to 0.05 to 0.2 °C/min.

Pore size distributions of Q-50 by MIP and TP that sample mass are different are shown in Fig.2. From the result of MIP, Q-50 has small range distribution and even pore structure. For TP, both large and small mass samples have larger distribution than MIP, and small mass sample has smaller distribution than large mass sample. it is thought that this difference is base on heat amount. Heat flow type DSC calculates heat quantity from difference of temperature between sample and reference. The reaction of large sample enlarges difference of temperature, a lot of time to return to static state is needed and distribution gets large. Also, Q-50 has larger distribution than Q-15 at same rate of temperature change. It is because of Pore radius is inversely relate to melting depression, influence of melt rate and heat amount appear dominantly in region of large diameter. But, these influences can be controlled by rate of temperature change and sample amount, and TP has possibility to obtained pore size distribution.

5. Conclusion

This study discuss that measurement condition and pore structure using primary material as porous silica and possibility of thermoporometry as measurement of pore size distribution.

Influences of melt rate of ice and heat amount extend distribution, but these influences are controllable to reduce rate of temperature change and sample amount, and TP has possibility to analyze pore structure.

6. Future work

It is thought that several approaches are needed to analyze cement and concrete.

(1) Hardened cement has wide pore size distribution, gel pore in 1nm~3nm, capillary pore in 3nm~200 μm. It necessary to correct experimental curve by time constant to control influence of melt rate of ice and heat amount.

(2) Cement includes several dissolved material. When these materials dissolved to pore water, change of surface tension, melting point and so on. It is necessary to search or control this influence.

(3) MIP is difficult to analyze week hardening body as deteriorated cement. It necessary to consider TP has possible application to analyze deteriorated concrete e.g. sulfuric acid attack and salt damage.

7. Publication

[Papers]

[Presentation]
(1) the 7th International Symposium on Cement & Concrete(oral, proceeding in press)
(2) The 11th Korea Japan joint seminar for Young Scientists on Construction Materials (oral)