Application Note B-TA1057

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B-TA1057 - Thermal behavior of water in hardened cement paste

Introduction

Portland cement hardened samples with different water-to-cement ratios were prepared, and differential scanning calorimetry (DSC) was used to measure the crystallization of water contained in the samples during cooling process and the melting during heating process, and the DSC results were compared.

Measurement and results

The samples were prepared by mixing and stirring commercially available Portland cement powder and water in weight ratios of 100:65 (W/C 65%), 100:50 (W/C 50%), and 100:35 (W/C 35%), and then leaving them to harden in water for 30 days. Approximately 15 mg of the hardened sample was cut out in block form and placed in an aluminum-sealed pan for DSC measurements.

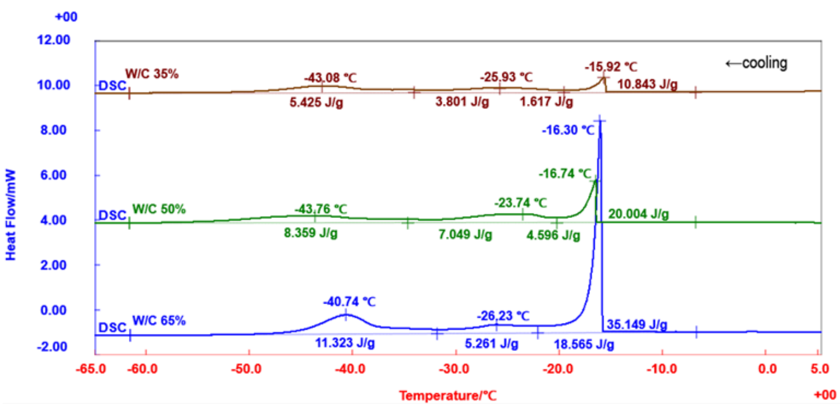

Figure 1 DSC measurement results (cooling process)

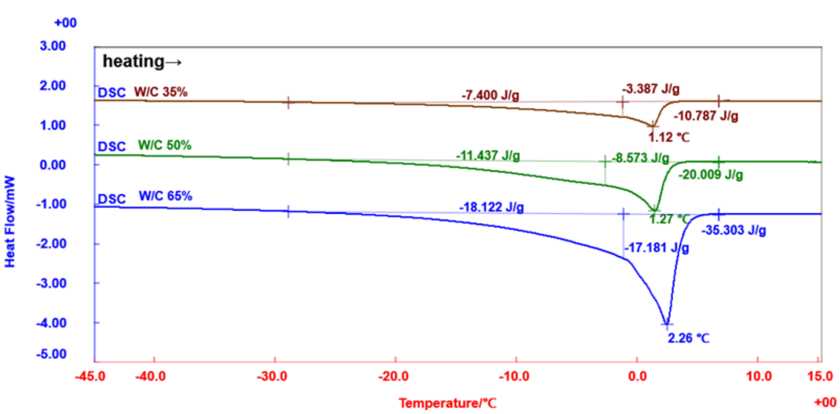

Figure 2 DSC measurement results (heating process)

Water in a substance can exist as bound water, which has structural interactions with the substance, or as free water, which has no interactions. Bound water is further classified into non-freezing water, which has strong interactions and does not crystallize (freeze) during the cooling process, and intermediate water, which is weakly affected and crystallizes at lower temperatures than free water.

In the present measurements, three exothermic peaks were observed for all samples during the cooling process, appearing at approximately −16 °C, −25 °C, and −40 °C. Even in the case of pure water, it is known that free water crystallizes below around −15 °C due to supercooling, and the peak around −16 °C is considered to be due to crystallization of free water in the hardened cement paste. The peaks at −25 °C and −40 °C are attributed to intermediate water, and the appearance of peaks in two temperature ranges suggests the presence of two types of intermediate water with different binding states.

The peak areas obtained from each DSC curve were separated into free water and intermediate water, and the free water ratio (free water energy/total energy) and intermediate water ratio (intermediate water energy/total energy) were calculated. These results are summarized in Table 1.

It can be seen that as the water content increases (i.e., as the cement content decreases), the proportion of free water increases, while the proportion of intermediate water decreases.

Table 1. DSC peak areas and ratios of free water and intermediate water (cooling process)

Energy J/g	W/C 35 %	W/C 50 %	W/C 65 %
TOTAL	10.84	20.00	35.15
Free water	1.62	4.60	18.57
Intermediate water 1	3.80	7.05	5.26
Intermediate water 2	5.43	8.36	11.32
Total intermediate water	9.23	15.41	16.58
Ratio in total energy %			
Free water	14.9	23.0	52.8

During the heating process, a broad endothermic peak and followed by a sharp consecutive peak are observed between -30°C and 0°C. The broad endothermic peak observed at low temperatures is considered to be attributed to the melting of intermediate water, and the sharp endothermic peak observed at high temperatures is attributed to the melting of free water. The peak areas and the calculated ratios of free water and intermediate water derived from them are summarized in Table 2.

Table 2 Peak areas and ratios of free water and intermediate water (heating process)

Energy J/g	W/C 35 %	W/C 50 %	W/C 65 %
TOTAL	10.79	20.00	35.30
Free water	3.39	8.57	17.18
Intermediate water	7.40	11.44	18.12
Ratio in total energy %			

Free water	14.9	23.0	52.8
Intermediate water	68.6	57.2	51.3

Comparing the results obtained from the cooling and the heating processes, there is a consistent tendency for the free water ratio to increase and the intermediate water ratio to decrease with increasing the water content (i.e. cement content decreases). However, the ratio of free water to intermediate water changes, and the peak shapes are different, suggesting that the interaction between water and hardened cement paste during the cooling process is different from the interaction during the heating process after freezing.

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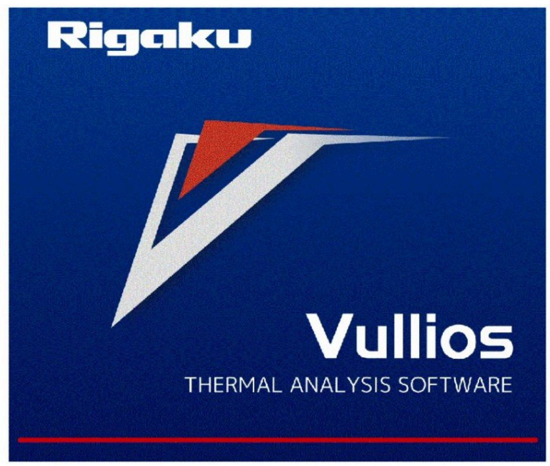

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Measurement and analysis software for Rigaku Thermal An alysis instruments