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Simultaneous TG/DTA DTG-60
Fourier Transform Infrared Spectrophotometer IRXross™, IRTracer™-100

Application News

Thermal Characterization and Quantification of Polymorphism in Calcium Carbonate Crystals

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User Benefits

- The thermal behavior of the crystal polymorphs of calcium carbonate can be investigated by the DTG-60.
- The crystal polymorphs of calcium carbonate can be analyzed in a short time using ATR FTIR measurements.
- Even in the presence of multiple crystalline polymorphs, it is possible to separate and quantify closely located peaks using differential spectra in FTIR.

■ Introduction

CO_2-absorbing concrete is an innovative construction material which is expected to be used to achieve carbon neutrality. CO_2 can be sequestered by a process of carbonizing the calcium in concrete and absorbing CO_2 by forming calcium carbonate, and hardening concrete. This can contribute to suppressing global warming.

Calcium carbonate has three crystal polymorphs, calcite, aragonite, and vaterite. Because differences in the particle size and particle shape also affect the strength of concrete, it is important to understand and control the ratio of these polymorphs. From the viewpoint of CO_2 fixation, the thermal behavior of crystal polymorphs is also important information for understanding the amount of fixed CO_2 and the duration of fixation by thermal analysis [1)].

In this article, a qualitative analysis and evaluation of the thermal characteristics of the polymorphs in calcium carbonate were carried out using a DTG-60 simultaneous TG/DTA, and quantitative analysis of the crystal polymorphs of calcium carbonate was conducted using a Fourier Transform Infrared Spectrophotometer IRTracer-100.

Fig. 1 Appearance of DTG-60 (Left) and IRTracer™-100 (Right)

■ Polymorphs of Calcium Carbonate

Calcium carbonate has three crystal forms: trigonal calcite, orthorhombic aragonite, and hexagonal vaterite. At normal temperature and normal pressure, calcite is a stable phase, aragonite is a metastable phase, and vaterite is an unstable phase. For this reason, calcite and aragonite, known as natural minerals primarily composed of calcium carbonate, correspond to relatively stable calcite and aragonite forms, respectively, but artificially-manufactured calcium carbonate also contains unstable vaterite.

■ Investigation of Thermal Behavior by DTG-60

To investigate the thermal behaviors of the polymorphs of calcium carbonate, calcite, vaterite, and aragonite were measured with a DTG-60 (Fig. 1, left). Table 1 shows the analysis conditions.

Table 1 Analysis Conditions of DTG-60

Instrument	: DTG-60
Heating rate	: 10 °C/min
Temperature range	: 30 °C - 1000 °C
Sample weight	: 30 mg
Atmosphere	: Nitrogen

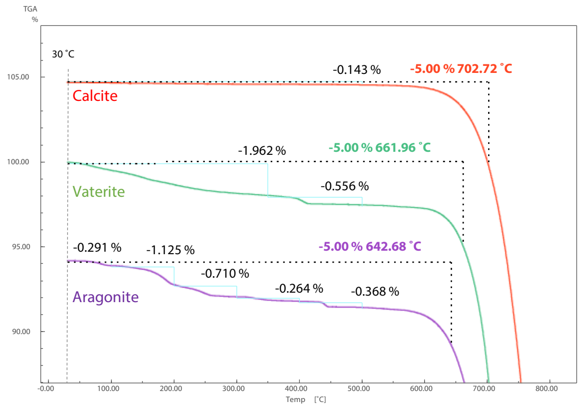

Fig. 2 TG Curves of Calcium Carbonate (3 Types)

Fig. 2 shows the thermogravimetric (TG) curves from 30 °C to 800 °C. The temperatures at which the sample weight decreased by 5 % were compared, standardized to the weights of the samples at 30 °C, at which the weight is unchanged. The temperatures for a 5 % weight reduction of the respective samples were 702.72 °C for calcite, 661.96 °C for vaterite, and 642.68 °C for aragonite, indicating that calcite has the highest heat resistance. It was also found that calcite shows a one-step weight reduction up to 500 °C, while vaterite shows a two-step weight reduction and aragonite shows multi-step weight reduction.

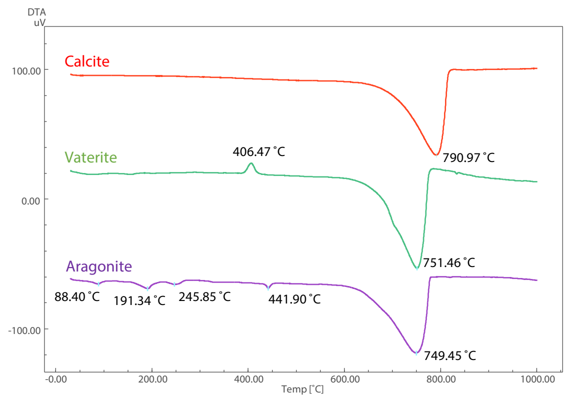

Fig. 3 DTA Curves of Calcium Carbonate (3 Types)

Fig. 3 shows the DTA curves from 30 °C to 1000 °C. Differences depending on the polymorphs of calcium carbonate could be seen in the endothermic/exothermic peaks observed from 30 °C to 600 °C, and in the endothermic peak temperature accompanying the decarboxylation process at temperatures above 750 °C.

Because each crystal form shows different TG and DTA curves, it is possible to distinguish the polymorphs of calcium carbonate by DTG measurement of calcium carbonate.

■ Quantitative Analysis by FTIR

Measurement of Infrared Spectra

Conventionally, a technique using an X-ray diffractometer (XRD) was the main stream in polymorphic analyses of cement, but infrared spectroscopy has attracted attention because it offers the advantages of ① the small sample amount (several 10 mg) used in the analysis, ② convenience, in that one measurement can be completed in a few minutes, and ③ detection of changes in the amorphous structure is possible, and application to analysis of the carbonation reaction of concrete and cement is expected [1]. Here, the infrared spectra of the three polymorphs of calcium carbonate measured with the DTG-60, together with cement, were measured by the single-reflection ATR method. To minimize the effects of water vapor and CO_2 in the atmosphere, the measurements were carried out after nitrogen purging in the instrument. Table 2 shows other detailed measurement conditions.

Table 2 FTIR Measurement Conditions

Instruments	: IRTracer-100, MicromATR (diamond)
Resolution	: 4 cm^{-1}
Accumulation	: 40 times
Apodization function	: Happ-Genzel
Detector	: DLATGS

Fig. 4 shows the infrared spectra of the three polymorphs of calcium carbonate and cement. Even in peaks that belong to the same vibrational mode, differences in the peak position could be seen, depending on differences in the polymorphs. Only in the cement sample, a peak could be observed at around 513 cm^{-1}.

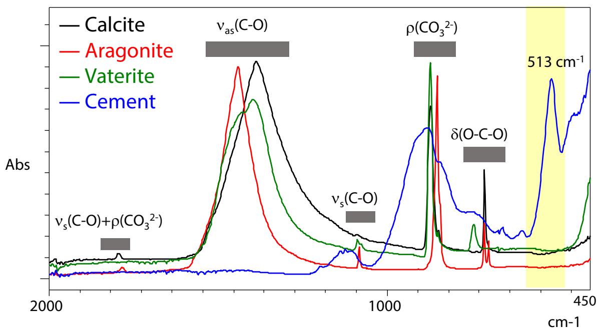

Fig. 4 Infrared Spectra of Polymorphs of Calcium Carbonate and Cement (Attribution of the peaks was done referring to Reference [2].)

Determination of Mass Ratio (Preparation of Calibration Curves)

From Fig. 4, it can be understood that the infrared spectra of the polymorphs of calcium carbonate are extremely similar. However, it is possible to acquire independent peaks of each polymorph, without losing quantitativity, by waveform separation by differentiation of each spectrum. Fig. 5 to Fig. 7 show the second derivative spectra of the infrared spectra of the three polymorphs of calcium carbonate and the peak positions used in quantitation. The peak top of the second derivative spectrum is a negative number, so the signs were inverted.

Here, the mixing ratio calculation method was used in quantitative determination of the mixing ratio. Details of the mixing ratio calculation method may be found in Application News No. A581.

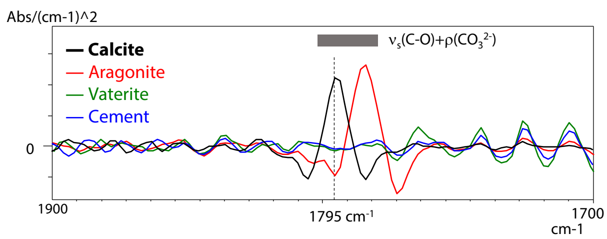

Fig. 5 Secondary Derivative Spectra of 3 Polymorphs of Calcium Carbonate and Cement and Peak Position (1795 cm^{-1}) Used in Quantitation of Calcite

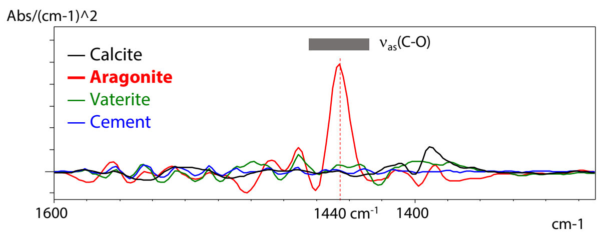

Fig. 6 Secondary Derivative Spectra of 3 Polymorphs of Calcium Carbonate and Cement and Peak Position (1440 cm^{-1}) Used in Quantitation of Aragonite

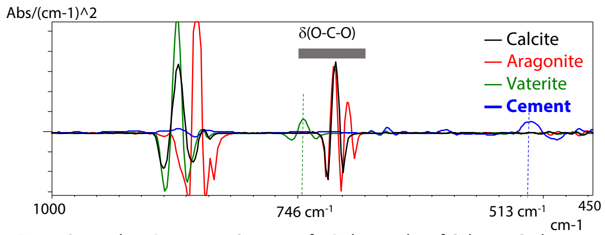

Fig. 7 Secondary Derivative Spectra of 3 Polymorphs of Calcium Carbonate and Cement and Peak Positions (740 m^{-1}, 513 cm^{-1}) Used in Quantitation of Vaterite and Cement

Table 3 shows the standard reference samples ① to ④ prepared by mixing the sample materials shown in Fig. 4, together with their mass ratios, for quantitation of the polymorphs of calcium carbonate in cement. Note that each of the standard samples was prepared so as to obtain a total weight of approximately 10 g.

Table 3 Standard Reference Samples and Mass Ratios (%) Used in Preparation of Calibration Curves

	Calcite	Aragonite	Vaterite	Cement
①	30 %	0 %	0 %	70%
②	0 %	30 %	0 %	70%
③	0 %	0 %	30 %	70%
④	10 %	10 %	10 %	70%

Each of the samples was measured 3 times, and the calibration curves of the mass ratios of each of the polymorphs in cement were prepared using a total of 12 spectra. Quantitation was carried out using the ratio of the respective polymorphs to cement on the abscissa, and the peak height ratio on the ordinate. Figs. 8 to 10 show the obtained calibration curves. Satisfactory correlations of 0.99 or higher were obtained for all the calibration curves.

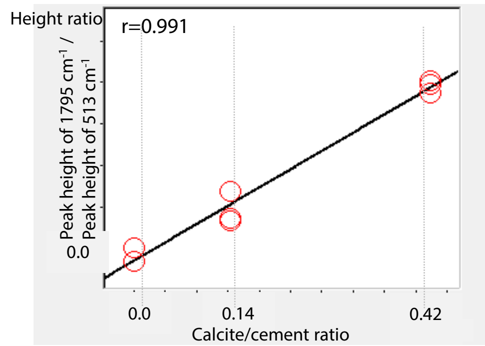

Fig. 8 Calibration Curve of Calcite Contained in Cement

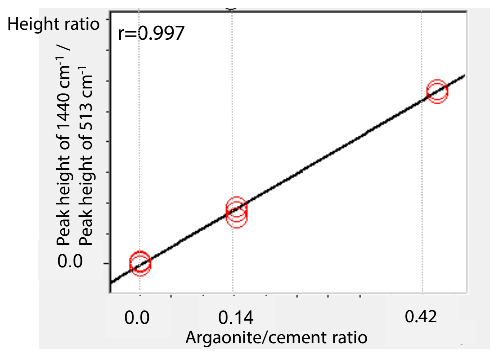

Fig. 9 Calibration Curve of Aragonite Contained in Cement

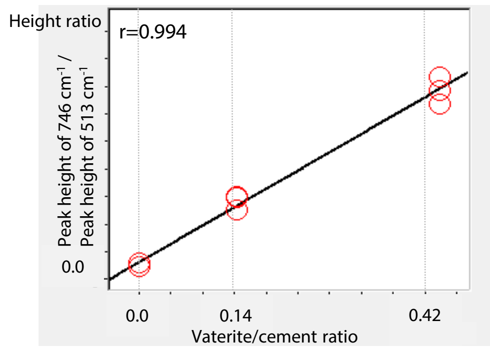

Fig. 10 Calibration Curve of Vaterite Contained in Cement

Quantitation of Mass Ratio (Mixing Ratio Calculation Method)

Quantitation of the mass ratios of the polymorphs contained in the simulated test materials was carried out using the calibration curves shown in Fig. 8 to Fig. 10. To minimize the effect of variations in the measurements, the simulated samples were measured 3 times. Table 4 shows the mass ratios of each of the polymorphs to cement obtained directly using the calibration curves.

Table 4 Results of Quantitation of Mass Ratios of Polymorphs to Cement in Simulated Sample

	Calcite	Aragonite	Vaterite
1st measurement	0.191	0.108	0.175
2nd measurement	0.199	0.119	0.243
3rd measurement	0.206	0.084	0.196
Average	0.199 $=w_{Cal/Cem}$	0.104 $=w_{Ara/Cem}$	0.204 $=w_{Vat/Cem}$

Use of the mixing ratio calculation method enables quantitative determination of the mass ratios of each of the polymorphs in samples containing different polymorphs.

Next, the results of quantitation of the mass ratios of the polymorphs to cement shown in Table 4 were converted to the mass ratios of the polymorphs and cement to the total weight of the sample. The following Eqs. (1) to (4) were used in the conversion.

$$w_{Cal/Total} = \frac{w_{Cal/Cem}}{1+w_{Cal/Cem}+w_{Ara/Cem}+w_{Vat/Cem}} \times 100 \qquad (1)$$

$$w_{Ara/Total} = \frac{w_{Ara/Cem}}{1+w_{Cal/Cem}+w_{Ara/Cem}+w_{Vat/Cem}} \times 100 \qquad (2)$$

$$w_{Vat/Total} = \frac{w_{Vat/Cem}}{1+w_{Cal/Cem}+w_{Ara/Cem}+w_{Vat/Cem}} \times 100 \qquad (3)$$

$$w_{Cem/Total} = \frac{1}{1+w_{Cal/Cem}+w_{Ara/Cem}+w_{Vat/Cem}} \times 100 \qquad (4)$$

Table 5 shows the predicted values and the actual measured values of the mass ratios of the polymorphs and cement to the total weight of the simulated sample. Here, the measured values were calculated using the mass when the simulated sample was prepared.

Table 5 Predicted Values
and Measured Values of Mass Ratios of Simulated Sample

	$w_{Cal/Total}$	$w_{Ara/Total}$	$w_{Vat/Total}$	$w_{Cem/Total}$
Predicted value	13.2 %	6.9 %	13.6 %	66.3 %
Measured value	13.6 %	6.8 %	11.4 %	68.2 %

As shown in this technique, the mixing ratio calculation method makes it possible to estimate the mass ratios of various polymorphs, even in samples containing multiple polymorphs.

Since samples can be measured simply, merely by pressing the sample powder against the ATR prism, analysis by the ATR method introduced here can be used as a simple quantitation method for the polymorphs of calcium carbonate in cement.

■ Conclusion

An evaluation of the thermal characteristics of the crystal polymorphs of calcium carbonate was conducted using a DTG-60 (simultaneous TG/DTA), and a quantitative analysis of the mass ratio of the different polymorphs of calcium carbonate was carried out with an IRTracer-100 Fourier transform infrared spectrophotometer (FTIR).

The measurements using the DTG-60 revealed that the polymorphs of calcium carbonate have high heat resistance in the order aragonite < vaterite < calcite. Differences were observed in the DTA curves of each of the polymorphs, indicating that it is possible to distinguish the polymorphs based on their DTA curves if they are not mixing substances.

In the measurements using the IRTracer-100, differences in the spectral shape of the infrared spectra of the polymorphs were confirmed. It was also found that the mass ratios of each of the polymorphs in samples containing multiple polymorphs can be quantitatively determined by a simple technique by differentiation of the infrared spectra and use of the mixing ratio calculation method.

Production and development of concrete with new added value, i.e., fixation of CO_2 by calcium carbonate, has attracted considerable attention. The analysis technique introduced here is expected to be a useful tool for the production and control of this type of concrete.

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2) Sarah Steiner, Barbara Lothenbach, Tilo Proske, Andreas Borgschulte, FrankWinnefeld, “Effect of relative humidity on the carbonation rate of portlandite, calcium silicate hydrates and ettringite,” Cement and Concrete Research 135 (2020) 106116

<Related Applications>

1. Application News No.A581, Quantitative Analysis of Recycled Plastics Using FTIR –Mixing Ratio Calculation Method–

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