ABSTRACT
The previous paper (Part 1) proposed the concept of "equivalent material age" that uses the Arrhenius relation and explained a method for long-term prediction of indoor volatile organic compound (VOC) concentration considering temperature dependence. This paper first describes the experiment conducted to validate the long-term concentration formula and the results of the experiment and reports on a comparison of the measured values obtained with the predicted values. The experiment was conducted by a method conforming to JIS A1901:2003. The material measured was formaldehyde. In the experiment, measurement was made in five cases involving different conditions. The measured changes over time in the emission factor obtained in the experiment in which temperature was varied over time tended to agree fairly with the predicted values, but differences began to appear at a certain point in the experiment. A likely reason for the occurrence of the differences was the influence of differences between individual materials (members). It is thought that if prediction accuracy is to be improved, it is necessary to use more than one test specimen for each experiment. The authors intend to investigate the influence of differences among individual specimens in order to enhance prediction accuracy.

KEYWORDS
Simplified long-term prediction, Emission through internal diffusion, Arrhenius relation, Equivalent material age, Chamber experiment

INTRODUCTION
The previous paper proposed the concept of equivalent material age defined by using the Arrhenius relation and explained a method for long-term prediction of indoor VOCs concentration in consideration of temperature dependence.

In this paper, the details and results of a series of experiments conducted verify the proposed formula for long-term concentration prediction are described first. Then, the results of comparison of the experimental results and prediction values are reported.

1 PREDICTION AND VERIFICATION PROCEDURE
In this study, prediction and verification are made, on the basis of the experimental results obtained, by following this procedure:
(1) On the basis of the results of an experiment on the emission factor of the building material under consideration conducted at three temperatures (15°C, 28°C, 35°C), checks are made to determine whether or not the Arrhenius relation holds true for the building material, and the temperature dependence coefficient $e$ is also calculated.
(2) A regression equation is derived from the experimental results for the emission factor at a constant temperature (28°C).
(3) The experimental results for the emission factor in the case where temperature is changed with time (15°C=>28°C=>35°C) are compared with the values predicted from the temperature dependence coefficient e and the regression equation obtained from the experiments mentioned in (1) and (2) above.

2  EXPERIMENTAL METHOD

2.1  Small chamber system and sampling method

Photo 1 shows the small chamber system used for the experiment. Figure 1 shows the configuration of the 20L chamber system. The experiment was conducted by a method based on JIS A 1901 (small chamber method). The product (specimen) loading factor was 2.2 m²/m³, and the air exchange rate was 0.5 changes per hour. Temperature and humidity were measured in the mix chambers. Changes in temperature with time were effected by changing the temperature settings for the constant-temperature chambers.

Table 1 shows the sampling method and the sampling conditions. The substance to be sampled is formaldehyde. The building materials used in the test were 12 mm thick, 164 mm by 164 mm five-ply flooring panels with UV coating. Photo 2 shows a flooring panel used in the test.

The formaldehyde emission factor was measured with a DNPH Silica sampler (GL-Pac mini AERO), and a high-performance liquid chromatographer (HPLC) was used for analysis.

<table>
<thead>
<tr>
<th>Substance to be sampled</th>
<th>Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampler</td>
<td>DNPH-Silica  (GL-Pak mini AERO)</td>
</tr>
<tr>
<td>Flow rate</td>
<td>167 mL/min</td>
</tr>
<tr>
<td>Time</td>
<td>108 minutes</td>
</tr>
<tr>
<td>Sample volume</td>
<td>18L</td>
</tr>
<tr>
<td>Number of samples</td>
<td>1</td>
</tr>
</tbody>
</table>

2.2  Preliminary study on humidity control under variable temperature conditions

In the experiment, temperature settings are changed with time. The ability of the experiment apparatus
to control humidity according to changing temperatures was evaluated in advance. Figure 2 shows changes in humidity in the chamber in the case where the temperature setting was changed stepwise (15°C<=>28°C<=>35°C) and humidity was controlled to 50±5%.

The experiment showed that when the temperature setting was changed, relative humidity in the chamber changed sharply and that it took about five hours for humidity to stabilize to 50±5%. When the temperature setting was changed from 28°C to 15°C, relative humidity in the chamber immediately rose to about 80%, indicating that the emission factor of the building materials was being affected. The emission factors at a relative humidity of 50% and in dry air were also compared at each temperature by using building materials identical to the ones used in the verification experiment. As a result, similar emission factors were indicated at 15°C and 28°C, while at 35°C slightly higher values were indicated at the relative humidity of 50%.

In view of all of these results, it was decided that in the case where emission factor measurement was conducted under variable temperature conditions, dry air be used in order to minimize changes in relative humidity.

2.3 Experimental cases

Table 2 shows the experimental cases. Figure 3 shows the experiment schedule. Cases 1 to 3 are experiments designed to determine whether or not the Arrhenius relation holds true for the building materials and calculate the temperature dependence coefficient $e$. The three temperature settings used were 15°C, 28°C and 35°C. Case 4 is an experiment designed to derive a regression equation for time-dependent changes in the emission factor at a constant temperature to be used as a basis for prediction. Temperature was set at 28°C. The measurement period was 28 days. In Case 5, which is an experiment designed for the verification of predicted values, temperature settings were changed stepwise (15°C<=>28°C<=>35°C). On and after day 1, the temperature settings were kept constant for three or four days. As a general rule, sampling was made three days after the temperature setting was changed, and a total of nine samplings were made during the period. The same conditions were used for Case 4, too.

In all cases, the test specimens placed in the chambers were not taken out until the end of the measurement period and were kept in the chambers while the measurements were conducted.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Period</th>
<th>Temperature</th>
<th>Relative humidity</th>
<th>Number of measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>1 day</td>
<td>15°C</td>
<td>50%</td>
<td>1</td>
</tr>
<tr>
<td>Case 2</td>
<td>1 day</td>
<td>28°C</td>
<td>50%</td>
<td>1</td>
</tr>
<tr>
<td>Case 3</td>
<td>1 day</td>
<td>35°C</td>
<td>50%</td>
<td>1</td>
</tr>
<tr>
<td>Case 4</td>
<td>28 days</td>
<td>28°C(constant)</td>
<td>50%</td>
<td>9</td>
</tr>
<tr>
<td>Case 5</td>
<td>28 days</td>
<td>15°C&lt;=&gt;28°C&lt;=&gt;35°C(changed)</td>
<td>No setting</td>
<td>9</td>
</tr>
</tbody>
</table>
3 EXPERIMENTAL RESULTS

3.1 Temperature and humidity
In Cases 1 to 4, temperature and humidity in the chambers were mostly kept at the set temperature plus or minus 0.5°C and the set humidity plus or minus 5%. Figure 4 shows changes over time in temperature and humidity in the mix chamber in Case 5 in which the temperature setting was varied. The numbers (1) through (4) in Figure 4 correspond to the enlarged views of time-dependent changes shown in Figure 5. Relative humidity remained 20% or less throughout the experiment. In Case 4 and Case 5, slight humidity fluctuations occurred temporarily under the influence of the opening of the constant-temperature chamber for sampling, but the set temperature and humidity were restored soon. Figure 5 shows, on a magnified time scale, time-dependent changes in temperature at different temperature settings. In the cases where temperature rose from 15°C to 28°C and from 28°C to 35°C, a steady state was reached in about 60 minutes. In the case where temperature fell from 35°C to 28°C, a steady state was reached in a shorter time (about 45 minutes). In the case, however, where temperature fell from 28°C to 15°C, the time required for reaching a steady state was about 180 minutes, which is about three to four times longer than the time required in the other cases.

3.2 Temperature dependence of the emission factor
Figure 6 shows the relationship between temperature and the emission factor ratio. The emission factor ratio has been normalized by using the 28°C experimental values. The emission factor ratio fell to about 25% at 15°C and rose to about 280% at 35°C. As a next step, the Arrhenius relation was applied. Out of the three experimental values obtained, two
values for the temperatures of 15°C and 35°C were used to calculate the temperature dependence coefficient \( e \) on the basis of the Arrhenius relation. The experimental values and the equation thus derived showed close agreement. The building materials, therefore, can be expressed by using the Arrhenius relation. The obtained value of the temperature dependence coefficient \( e \) was 10861.8 K.

3.3 Changes in the emission factor over time

1. Changes over time in the emission factor at constant temperature (28°C)

Figure 7 shows changes over time in the emission factor decrement at a constant temperature (28°C) (Case 4). The emission factor decrement has been normalized by using the experimental values obtained on day 1. The emission factor decrement was higher at an earlier stage, and it became smaller with time. Logarithmic approximations showed close agreement within the range covered by the measurement, and the following regression equation was derived:

\[
E(t)/E(1) = -28.3 \ln(t) + 98.9
\]

2. Changes over time in the emission factor under variable temperature conditions

Figure 8 shows changes over time in the emission factor decrement in the case where temperature was varied (Case 5). As temperature rose and fell, the emission factor increased and decreased repeatedly and tended to be attenuated as time passed. The value at 28°C on day 28 was about 20% of the value on day 1.
4 CONCENTRATION PREDICTION

4.1 Equivalent material age

Figure 9 shows the relationship between the real material age \( T_r \) and the equivalent material age \( T_e \). The real material age is the same as the period (days) during which the building materials were exposed to a constant temperature of 28°C. The equivalent material age varies with temperature according to the Arrhenius relation determined earlier. The changes are slow at 15°C and are accelerated at 35°C.

4.2 Comparison of measured emission factors under variable temperature conditions with predicted values

Figure 10 compares experimental values and prediction values of changes over time in the emission factor decrement. The experimental values and prediction values tend to show fair agreement until day 8. On day 12, however, the experimental values are slightly greater than the prediction values, and that tendency continues thereafter. The differences between the measured values and the calculated values tended to increase if the temperature to which the specimens were exposed was high, and, conversely, they tended to decrease if the exposure temperature was low. Day 12 was during the period in which the test specimens were being exposed to a temperature of 35°C. Day 18 was during the period in which the specimens were being exposed to 15°C. As shown, the differences between the measured values and the calculated values are smaller than during the period of exposure to 35°C.

A likely reason for this difference is the influence of differences among structural members. The experimental values in this study were obtained from a single test specimen. It is therefore likely that both the experimental values used for the prediction and the experimental values used for the verification were influenced by differences among individual specimens. For example, the test conditions used in the case where temperature was kept constant at 28°C and the test conditions used on day 1 in the case where temperature was varied from 28°C were identical, but the emission factor values showed differences by a factor of about 1.6.

It is possible that among the experimental values used to determine the temperature dependence coefficient \( e \), the effective diffusion coefficient \( D_{VOC} \) at 35°C was too large. It is thought likely, therefore, that the prediction values indicated considerably fast aging, showing emission factor decrements lower than the experimental values on day 12. The influence of this difference remained after day 12. It is also possible that the experimental values of the emission factor decrement at the constant temperature of 28°C which were used as the basis for prediction were too large. On the contrary, it is also possible that the amounts of attenuation of the emission factor in the experiment (Case 5) designed for the verification of temperature changes were smaller than the predicted values because of differences among individual specimens.

In order to enhance prediction accuracy, it is necessary to use more than one test specimen for each experiment. When the temperature dependence coefficient \( e \) is to be determined, it is a better practice
to increase the number of tests, particularly tests involving higher temperatures.

Figure 9 Relationship between real material age and equivalent material age

Figure 10 Comparison between predicted values and experimental values

5 CONCLUSION
This paper has described the details and results of a series of experiments conducted to verify long-term concentration predictions and has reported on the results of comparison between experimental values and predicted values. The findings of this study are summarized below.

(1) Comparison of the measured values of changes over time in the emission factor obtained in the experiment in which temperature was varied over time (15°C<=>28°C<=>35°C) with predicted values has shown that fair agreement was shown at early stages, but differences began to appear at later stages.

(2) A likely reason for the occurrence of the differences mentioned above is the influence of differences among individual structural members. The experimental values in this study were obtained from a single test specimen. It is therefore likely that both the experimental values of the temperature dependence coefficient $e$ and the time-dependent changes under constant temperature conditions used for the prediction and the experimental values used for the verification were influenced by the differences among individual specimens.

(3) In order to enhance prediction accuracy, it is necessary to use more than one test specimen for each experiment. When the temperature dependence coefficient $e$ is to be determined, it is a better practice to increase the number of tests, particularly tests involving higher temperatures.
The authors intend to investigate the influence of differences among individual test specimens in order to further enhance prediction accuracy. The authors are also thinking of conducting verification for various chemicals contained in a wide variety of building materials in order to put the prediction method to practical use.

REFERENCES
1. JIS (Japanese Industrial Standards) A 1901:2003, Small chamber method - Determination of the emission of volatile organic compounds and aldehydes for building products