## TRANSFER IN CURING FINE-GRAIN CONCRETE BY

VARIOUS MODES OF THERMOHUMIDITY TREATMENT
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The parameters of internal mass and heat transfer in a cement mixture are calculated from kinetic curves of the heat treatment, with the aid of thermodynamic functions characterizing irreversible processes.

The transfer of energy and moisture in the concrete curing process can be described approximately by the system of equations which A. V. Lykov has proposed in [1]:

$$
\begin{gather*}
\frac{\partial t}{\partial \tau}=a \nabla^{2} t+\frac{\varepsilon r}{c} \cdot \frac{\partial u}{\partial \tau}  \tag{1}\\
\frac{\partial u}{\partial \tau}=a_{m}\left[\nabla^{2} u+\delta \nabla^{2} t\right] \tag{2}
\end{gather*}
$$

The exothermal effects are accounted here, of course, by lumping them together into the last term of Eq. (1), as has been done in $[7,8]$.

A unique solution to this system was expressed in terms of locally measured temperature

$$
\begin{equation*}
t\left(x_{1}, \tau\right)=t_{1}(\tau)=Э_{1}(\tau) ; \quad t\left(x_{2}, \tau\right)=t_{2}(\tau)=\ni_{2}(\tau) \tag{3}
\end{equation*}
$$

and moisture content

$$
\begin{equation*}
u\left(x_{3}, \tau\right)=u_{1}(\tau)=\ni_{3}(\tau) ; \quad u\left(x_{4}, \tau\right)=u_{2}(\tau)=\ni_{4}(\tau) \tag{4}
\end{equation*}
$$

In the experiment reported here we observed an overlapping of temperature and moisture content test points $x_{1}=x_{3}$ and $x_{2}=x_{4}$.

In dimensionless form this system of transfer equations becomes

$$
\begin{gather*}
\frac{\partial T}{\partial \mathrm{Fo}}=\frac{\partial^{2} T}{\partial N^{2}}+\varepsilon \mathrm{Ko} \frac{\partial u}{\partial \mathrm{Fo}},  \tag{5}\\
\frac{\partial u}{\partial \mathrm{Fo}}=\mathrm{Lu}\left[\frac{\partial u}{\partial N^{2}}+\operatorname{Pn} \frac{\partial^{2} T}{\partial N^{2}}\right], \tag{6}
\end{gather*}
$$

where the dimensionless temperature $T$ and the dimensionless moisture content $u$ are referred to the numerical temperature difference $t_{f}-t_{0}$ and to the initial moisture content $u_{0}$ respectively:

$$
\begin{equation*}
T\left(N, \mathrm{~F}_{0}\right)=\frac{t(x, \tau)-i_{0}}{t_{\mathrm{f}}-t_{0}}, u\left(N_{\mathrm{I}} \mathrm{Fo}\right)=\frac{u(x, \tau)}{u_{0}} \tag{7}
\end{equation*}
$$

The dimensionless coordinate $N$ is referred to the distance between measuring instruments, $b=x_{2} \rightarrow x_{1}$

$$
\begin{equation*}
N=\frac{x-x_{1}}{x_{2}-x_{1}} \tag{8}
\end{equation*}
$$

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TABLE 1. Experimental Values and the Derivatives

| $\begin{aligned} & E \\ & \sum_{n}^{n} \end{aligned}$ |  |
| :---: | :---: |
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| $\begin{aligned} & x \\ & \vdots \\ & \end{aligned}$ | 8.:. <br> 0000000000000000000 |
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|  |  |

The same characteristic dimension has been chosen for the Fo number. The $\varepsilon$ Ko number and the Pn number have been defined according to [2].

The conditions for a unique solution in the dimensionless form are

$$
\begin{gather*}
\frac{t\left(x_{1}, \tau\right)-t_{0}}{t_{\mathrm{k}}-t_{0}}=T(0, \mathrm{Fo})=\ni_{1}(\mathrm{Fo}),  \tag{9}\\
\frac{t\left(x_{2}, \tau\right)-t_{0}}{t_{\mathrm{si}}-t_{0}}=T(1, \mathrm{Fo})=\ni_{2}(\mathrm{Fo})  \tag{10}\\
\frac{\ell\left(x_{1}, \tau\right)}{u_{0}}=u(0, \mathrm{Fo})=Э_{3}(\mathrm{Fo})  \tag{11}\\
\frac{u\left(x_{2}, \tau\right)}{u_{0}}=u(1, \mathrm{Fo})=Э_{4}(\mathrm{Fo}) \tag{12}
\end{gather*}
$$

These empirical functions were identified continually throughout the entire test.

The solution to the transfer equations on the basis of local temperature and moisture content measurements can be represented, as has been done in [2, 3], by sums of series terms in the derivatives of the empirical functions:

$$
\begin{align*}
& T(N, \mathrm{Fo})=\sum_{i=1}^{n} \sum_{n=0}^{\infty} \exists_{i}^{(n)}(\mathrm{Fo}) P_{n i}(N),  \tag{13}\\
& u(N, \mathrm{Fo})=\sum_{i=1}^{n} \sum_{n=0}^{\infty} \exists_{i}^{(n)}(\mathrm{Fo}) Q_{n i}(N), \tag{14}
\end{align*}
$$

where $P_{n i}(N)$ and $Q_{n i}(N)$ are divergent polynomials in the problem, their matrix being

$$
\left.\begin{array}{ccccccc}
P_{01} & P_{11} & \ldots & Q_{01} & Q_{11} & \ldots & . \\
P_{02} & P_{12} & \ldots & Q_{02} & Q_{12} & \ldots & . \\
P_{03} & P_{13} & \ldots & . & Q_{03} & Q_{13} & \ldots \tag{15}
\end{array}\right) .
$$

In a form which is dimensional with respect to time, this solution for the temperature and the moisture content can be written down as follows:

$$
\begin{align*}
& T(N, \tau) \leftrightharpoons\left[T_{1}(\tau) P_{01}(N)+T_{2}(\tau) P_{02}(N)\right]+\left[T_{1}^{\prime}(\tau) P_{11}(N)\right. \\
& \left.+T_{2}^{\prime}(\tau) P_{12}(N)\right] \frac{b^{2}}{a}+\left[u_{1}^{\prime}(\tau) P_{13}(N)+u_{2}^{\prime}(\tau) P_{14}(N)\right] \frac{b^{2}}{a}+\ldots,  \tag{16}\\
& \\
& u(N, \tau)=\left[u_{1}(\tau) Q_{03}(N)+u_{2}(\tau) Q_{04}(N)\right]+\left[T_{1}^{\prime}(\tau) Q_{11}(N)\right.  \tag{17}\\
& \div \\
& \left.\div T_{2}^{\prime}(\tau) Q_{12}(N)\right] \frac{b^{2}}{a}+\left[u_{1}^{\prime}(\tau) Q_{13}(N)+u_{2}^{\prime}(\tau) Q_{14}(N)\right] \frac{b^{2}}{a}+\cdots
\end{align*}
$$

A temperature measurement at point N makes it possible to determine the magnitude of the empirical difference

$$
\begin{equation*}
\Delta\left(N, N_{1}, N_{2}, \tau\right)=T(N, \tau)-\left[T_{1}(\tau) P_{01}+T_{2}(\tau) P_{02}\right] \tag{18}
\end{equation*}
$$

and the test quantities related to the local heating rate as follows:

$$
\begin{align*}
& \eta(\tau)=T_{1}^{\prime}(\tau) P_{11}+T_{2}^{\prime}(\tau) P_{12},  \tag{19}\\
& \xi(\tau)=u_{1}^{\prime}(\tau) P_{13}+u_{2}^{\prime}(\tau) P_{14} . \tag{20}
\end{align*}
$$

With this notation, the temperature distribution (16) becomes - to the first approximation -

$$
\begin{equation*}
\eta \frac{b^{2}}{a}+\xi \frac{b^{2}}{a} \varepsilon K o=\Delta \tag{21}
\end{equation*}
$$

where

$$
\begin{align*}
\eta= & T_{1}^{\prime}(\tau) \frac{N(N-1)}{2}\left[\frac{2}{3}-\frac{N}{3}\right] \\
& +T_{2}^{\prime} \frac{N(N-1)}{2}\left[\frac{N}{3}+\frac{1}{3}\right],  \tag{21a}\\
\xi= & u_{1}^{\prime}(\tau) \frac{N(N-1)}{2}\left[\frac{N}{3}-\frac{2}{3}\right] \\
& +u_{2}^{\prime} \frac{N(N-1)}{2}\left[-\frac{N}{3}-\frac{1}{3}\right] . \tag{21b}
\end{align*}
$$

In order to determine the thermal diffusivity $a$ and the complex $\varepsilon$ Ko number, one must differentiate both sides of Eq. (21) with respect to time:

$$
\begin{equation*}
\eta^{\prime} \frac{b^{2}}{a}+\xi^{\prime} \frac{b^{2}}{a} \varepsilon K_{0}=\mathrm{A}^{\prime} \tag{22}
\end{equation*}
$$

and for the system of Eqs. (21), (22) one must define the arguments of the characteristic Massye-Gibbs functions:

$$
\begin{equation*}
z_{\mathrm{a}}=\eta / \xi ; \zeta=\Delta / \xi . \tag{23}
\end{equation*}
$$

For the thermal diffusivity $a$ we then obtain the expression:

$$
\begin{equation*}
a=b^{2} \frac{\partial z_{\mathrm{a}}}{\partial \zeta} \tag{24}
\end{equation*}
$$

and for the complex quantity:

$$
\begin{equation*}
\varepsilon K o=z_{\mathrm{a}}-\zeta \frac{\partial z_{\mathrm{a}}}{\partial \zeta} \tag{25}
\end{equation*}
$$

By complete analogy, if for the moisture content one defines the empirical quantity

$$
\begin{equation*}
z_{j}=\frac{b^{2}}{a} \cdot \frac{\omega}{\xi}, \tag{26}
\end{equation*}
$$

with

$$
\begin{equation*}
\omega=\left\{u(N, \tau)-\left[u_{1}(\tau) Q_{03}(N)+u_{2}(\tau) Q_{04}(N)\right]\right\}-\frac{a}{b^{2}}, \tag{27}
\end{equation*}
$$

then approximation of the moisture field (17) will yield expressions for the Pn number and the Lu number:

$$
\begin{equation*}
\mathrm{Pn}=-\frac{\partial z_{p}}{\partial z_{\mathrm{a}}}, \mathrm{Lu}^{-1}=z_{p}-\zeta \frac{\partial z_{p}}{\partial \zeta} \tag{28}
\end{equation*}
$$

In order to determine the transfer parameters, the authors have performed the following experiment. Specimens of cement mixture (fine-grain concrete) $200 \times 200 \times 60 \mathrm{~mm}$ large with a steel grid reinforcement consisting of 6 mm in diameter rods spaced $50 \times 50 \mathrm{~mm}$ apart were placed, after having been poured into molds, inside an apparatus containing a vapor chamber and an electromagnetic chamber. The procedure and the techniques of this experiment are described thoroughly in [4]. Evaporation of the moisture occurred only at the upper surface of a specimen, i.e., an asymmetrical uniform mode of mass transfer was observed. The local temperatures and moisture contents of six layers were determined continually. The
TABLE 2. Arguments of the Characteristic Functions and Parameters of the Internal Transfer

| Method of heat treatment | H | 7 | $\bar{\square}$ | $z_{\text {a }}$ | $\zeta$ | $z_{a}^{\prime}$ | $\xi^{\prime}$ | $a \cdot 10^{4}$ | عKo | ${ }^{2} p$ | $z_{p}^{\prime}$ | Lu | $\mathrm{Pr}_{\mathbf{n}}$ | $8 \cdot 10^{3}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Electromagnetic heat treatment | 0,0 | 20,0 | 0,1450 | 8,42 | 0,19 | 25,80 | 1,40 | 46,1 | 4,92 | 0,00 | -18,50 | 0,398 | 0,717 | 0,174 |
|  | 0,05 | 27,4 | 0,1446 | 10,00 | 0,27 | 19,28 | 1,26 | 39,8 | 5,87 | $-0,876$ | -15,808 | 0,399 | 0,823 | 0,2 |
|  | 0,10 | 37,1 | 0,1440 | 11,00 | 0,33 | 15,20 | 1,18 | 32,2 | 6,74 | $-1,850$ | -13,36 | 0,532 | 0,878 | 0,212 |
|  | 0,15 | 46,4 | 0,1432 | 11,30 | 0,38 | 13,00 | 1,08 | 30,1 | 6,63 | $-2,310$ | $-9,00$ | 0,563 | 0,692 | 0,168 |
| Vapor heat treatment | 0,0 | 20.0 | 0,1450 | $-9,4$ | 0,00 | 30,0 | 1,55 | 48,0 | 0,00 | 0,00 | 0,00 | $\infty$ | 0;00 | 0,00 |
|  | 0,05 | 25,0 | 0,1453 | -8,0 | 0,07 | 27,8 | 1,62 | 42,7 | -8,119 | 0,00 | -19,68 | 1,170 | 0,710 | 0,172 |
|  | 0,10 | 31,1 | 0,1460 | -6,4 | 0,155 | 26,8 | 1,83 | 36,8 | -8,680 | $-1,14$ | -39,52 | 0,463 | 1,470 | 0,356 |
|  | 0,15 | 43,7 | 0,1470 | $-5,2$ | 0,204 | 26,4 | 2,00 | 33,0 | -7,890 | $-2,92$ | -54,16 | 0,362 | 2,050 | 0,495 |
|  | 0,20 | 54,1 | 0,1484 | -4.0 | 0,320 | 24,0 | 2,15 | 28,0 | -7,380 | $-8,42$ | $-72,5$ | 0,435 | 3,020 | 0,73 |

Note. Mean-integral temperature $\overline{\mathrm{t}}(\tau),{ }^{\circ} \mathrm{C}$ mean-integral moisture content $\overline{\mathrm{u}}(\tau), \mathrm{kg} / \mathrm{kg}$.
local moisture contents were measured by the nondestructive method of irradiation with gamma quanta from a $\mathrm{Tm}^{170}$ isotope source. For this purpose, during their heat treatment, the specimens were transported on a special platform along the vertical axis of the chamber and the collimated gamma beam was aligned with a $\pm 0.3 \mathrm{~mm}$ precision [5]. The local temperatures were measured with copper-constantan thermocouples made of 0.2 mm diameter wire.

Using this method, measurements could be made without disrupting the continuity of material during its curing.

The thermohumidity treatment followed the $4+4+3+3 \mathrm{~h}$ cycle (holding before treatment + heating from $20^{\circ} \mathrm{C}$ to $80^{\circ} \mathrm{C}+$ isothermal treatment at $80^{\circ} \mathrm{C}+$ cooling to $40^{\circ} \mathrm{C}$ ). The ambient relative humidity was $85-90 \%$ in the chambers.

The thermohumidity treatment consisted of adding saturated vapor in the vapor chamber or of heating the ferromagnetic trays (bases) under the mold and the reinforcement grid in the electromagnetic chamber at a field intensity of 200 Oe .

The kinetic curves depicting this thermohumidity treatment of the cement mixture are shown in [4].
Calculations were made using the temperatures and moisture contents measured at the centers of surface layers, at a distance 5 mm from the top and the bottom surface of a specimen, then at 10 mm steps the center of the bottom layer. The dimensionless coordinates of the respective layer centers were

$$
N_{1}=\frac{0-0}{50-0}=0 ; \quad N_{2}=\frac{50-0}{50-0}=1 ; \quad N=\frac{10-0}{50-0}=0.2 .
$$

The initial temperature of the material was $20^{\circ} \mathrm{C}$, the maximum temperature (on the isotherm) was $80^{\circ} \mathrm{C}$. The temperature difference $\Delta t=80-20=60^{\circ} \mathrm{C}$ was used as the reference scale for the Pn numbers and the $\varepsilon$ Ko numbers. The dimensionless unit of time was referred to $10 \mathrm{~h}: \mathrm{H}=\boldsymbol{\tau}(\mathrm{h}) / 10$.

The derivatives of temperature and moisture content were calculated according to the rules of discrete differentiation [6]. "Limit" formulas, by which derivatives to the left and to the right can be determined from three test values of temperature and moisture content, were used for the end points and the inflection points of the curves. An interpolation procedure by which derivatives can be determined from four test values was found suitable for the neighboring points.

Values of the empirical moisture content and temperature functions in dimensionless form, as well as their derivatives, are all shown in Table 1. As the values of $u_{m}$ and $T_{m}$ are taken here the local moisture contents and temperatures $u_{m}=u_{2}, T_{m}=T_{2}$ for the vapor-heat treated specimen and $u_{m}=u_{4}, T_{m}=T_{4}$ for the electromagnetically heat treated specimen.

The numerical values calculated for the arguments of the characteristic functions $z_{a}, \zeta, z_{p}$ and their derivatives, as well as the values of the thermal diffusivity $a$ and of $L u, P n, \varepsilon K o$ numbers, are all given in Table 2.

For the period in which the temperature rises, the values of said quantities are given in Table 2 from $\mathrm{H}=0$ to $\mathrm{H}=0.20$. Beginning at $\mathrm{H}=0.20$ and until the end of the heating period the following inequality holds true:

$$
\frac{\partial z_{\mathrm{a}}}{\partial \zeta}<0
$$

In this case it is impossible to calculate the thermal diffusivity, because the character of the bond between moisture and material changes during heat treatment.

During the initial period of heat treatment, moisture in the concrete is bonded to dispersed colloidal particles by adsorptive and osmotic forces. At about $1-1.5 \mathrm{~h}$ after the heat treatment has begun, there takes place an intensive formation of a capillary structure characterized by a sharp decrease of the mass transfer potential. As capillaries are produced within the forming cement rock structure, a capillary bond between moisture and material begins to predominate.

Inequality (29) is also valid because during this period (at a temperature level of about $60^{\circ} \mathrm{C}$ ) the cement hydration reaction becomes quite perceptibly exothermal.

An analysis of the results (Table 2) shows that the thermal diffusivity $a$ decreases from the very beginning of the process, but its absolute value is somewhat greater during vapor-heat treatment and this is probably due to condensation at the material surface and due to the moisture transfer through it.

The magnitude of the temperature gradient (Table 2) is somewhat smaller during electromagnetic heating, as a result of a more uniform distribution of temperature fields here than during vapor-heat treatment.

During electromagnetic heat treatment moisture is removed, which has to do with heat absorption inside the material. The Kossovich numbers are then positive.

During vapor-heat treatment the Ko numbers are negative, as a result of condensation and molar vapor transfer into the bulk of the material, which is equivalent to an emergence of a positive internal heat source.

According to the calculated data, the values of the Lu number and of the Pn number during heat treatment vary considerably depending on the method by which the heat is supplied, and this indicates that the mechanism of mass and heat transfer is different in each case.

## NOTATION

| $\frac{t}{t}$ | is the temperature; |
| :--- | :--- |
| is the mean-integral temperature; |  |
| $t_{0}$ | is the initial temperature of the material; |
| $t_{f}$ | is the final temperature of the material; |
| $\frac{u}{u}$ | is the moisture content; |
| $u_{0}$ | is the mean-integral moisture content; |
| $\mathbf{r}$ | is the latial moisture content in the material; |
| $c$ | is the specific heat; |
| $\varepsilon$ | is the phase-transformation number; |
| $a_{m}$ | is the thermal diffusivity of moisture; |
| $\delta$ | is the temperature gradient. |

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