Lothenbach’s Model of Von Mises Stress Distribution in Portland Cement in Curing and Temperature Gradient Conditions

Yu A Abzaev¹, A I Gnyrya¹ and S V Korobkov¹
¹Tomsk State University of Architecture and Building, 2, Solyanaya Sq., 634003, Tomsk, Russia

E-mail: korobkov_1973@mail.ru

Abstract. The paper presents the two-dimensional Lothenbach’s model of Portland cement curing based on the finite element method. The cement curing lasts for 7 days in the temperature gradient conditions ranging from 65 to −20 °C. A cement rod 7×70 cm in size is used for modelling the temperature and von Mises stress distributions. It is shown that in the temperature gradient and curing conditions, the stress maximum in Portland cement shifts toward the hot edge of the cement rod and exceeds the minimum stress level more than two times. The stress growth is significant at the interfaces between the concrete timber and the cement rod, especially at its cold edge. Such a distribution of von Mises stress is connected with the heat flow generation and their superposition with reverse heat flows. At the interfaces, superposition of the negative heat flows generates higher stresses, than superposition of the positive heat flows. The concrete timber and the interface stability are the additional factors that increase the stress level and contribute to the fracture of the pore walls.

1. Introduction
In works [1–6] Lothenbach, et al. consider a thermodynamic model of dissolution of clinker minerals, aqueous composition of the pore space, product sedimentation as a function of hydration kinetics. The curing process modelling uses the GEMS-PSI geochemical code [2] and the adapted thermodynamic database CEM [3]. Well studied is the kinetics of the elemental and phase composition, water-cement ratio, activation energy of the dissolution of clinker phases, heat generation in forming the intermediate and final products, bound moisture in isothermal conditions. Using the hydration model proposed by Parrot and Killoh [7], the detailed description of the indicated parameters allows constructing approximating dependences of the hydration rate at a stage of new phase nucleation and the diffusion process of the hydration product growth. The model, however, does not consider the mechanisms of cement thermal curing under the temperature gradient conditions, which form due to the cement laying temperature, exothermic thermal processes and ambient temperature.

This work focuses on the early age behavior of cement in the temperature gradient conditions using the coupled multi-physics model. The investigated Portland cement is similar to that manufactured at the Topki Cement Plant (the Kemerovo region, Russia).
2. Model of Portland cement hydration

The curing mechanism of Portland cement in difficult conditions of heat and mass transfer can be predicted by modeling the thermal stress growth due to the operation of thermal sources and mechanisms of new phase formation during the hydration process. After cement setting, the distribution of the effective heat flows induced by the external temperature gradients and thermal sources can be considered in the approximation of a homogeneous medium or in terms of the diffusion mechanisms. The early age behavior of Portland cement relates to the multi-physics problem of interconnection between heat flows and structural mechanics [8, 9]. Assuming that during early-age curing the heat redistribution is determined by thermal conductivity, the governing is the equation with a volumetric thermal source:

\[ C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[ k(T) \frac{\partial T}{\partial x} \right] + \frac{\partial q(t)}{\partial t}, \]

where \( C_p \) is the specific heat capacity, \( \rho \) is the density, \( k(T) \) is the thermal conductivity coefficient, \( q \) is the thermal source, which is the time and space function.

The thermal conductivity coefficient depends on the moisture content and temperature [3, 4, 10]. Here, we assume that this coefficient is constant. The main thermal sources include chemical reactions, which occur owing to the hydration process on cement grains. The hydration reaction is exothermic and leads to a notable heat generation. The water diffusion through the hydrate layer is the dominant mechanism that determines the hydration kinetics. In the framework of the diffusion processes, the hydration products resulting from chemical reactions and mass transfer in cements can be described by the hydration \( \alpha(t) \), which is associated with the hydrated cement imbalance in real time \( t \), and is a measure of heat released during hydration. The imbalance of free and bound moisture in hydrates is the driving force of the hydration product growth [10–15]. With increasing temperature, the process of binding free water is enhanced by thermal activation. Since the affinity for the formation of hydrates is positive and proportional to the heat release \( Q(t) \), hydration can be written as [10–14]:

\[ \alpha(t) = q(t) / Q_{\text{max}}, \]

where \( Q_{\text{max}} \) is the internal latent heat resulting from complete hydration, \( q(t) \) is the thermal source, which is a function of real time \( t \).

During hydration, the hydrate layer increases and affects the moisture diffusion rate. Hydration is proportional to the normalized affinity and the temperature factor, which are taken into consideration in the Arrhenius relation. The models proposed in works [1–3] are based on the model designed in [7] and describe the early formation of hydration products, growth in diffusion, and the hydrate shell formation. The approximation parameters of Lothenbach’s model [1–7] are obtained from in-depth experimental research and summarized in table 1. The diffusion equation in Lothenbach’s model is written as

\[ R_i \frac{K_2 (1 - \alpha (t))^{2/3}}{1 - (1 - \alpha(t))^{1/3}}, \]

where \( R_i \) is the hydration constant, \( \alpha_i \) is hydration, \( K_2 \) is the approximation parameter.

| Table 1. Lothenbach’s model parameters [1–3]. |
|-----------------------------------------------|
| Clinker minerals | Alite | Belite | Aluminate | Aluminoferrite |
| Approximation parameter | 0.05 | 0.02 | 0.04 | 0.015 |
| Activation energy (kJ/mol) | 41.57 | 20.785 | 54.040 | 34.087 |
| Weight (g) | 64.6 | 9.3 | 7.4 | 7.8 |
Hydration is defined by
\[
\frac{\Delta x(t)}{\Delta t} = R_t
\]
and affected by the water-cement ratio \( f(w/c) \):
\[
f(w/c) = (1 + 4.444w/c - 3.333 \times (t))^4
\]
and temperature. As the approximating equation (2) for the hydration constant is obtained at room temperature, the temperature dependence of hydration can be written as
\[
\frac{\partial \alpha(T(t))}{\partial t} = R(T_1) \cdot f(w/c) \cdot \exp(\frac{T_1 - T(t)}{RT(t)} E_a),
\]
where \( T(t) \) is the temperature in real time \( t \), \( R \) is the gas constant, \( T_1 = 20 \) °C, \( E_a \) is the activation energy ranging between 35 and 50 kJ/mol. Hydration as a measure of heat is connected with the thermal source (equation (1)). After this, we derive from equation (3):
\[
\frac{\partial q(t)}{\partial t} = \rho Q_{\text{max}} \frac{\partial \alpha(t)}{\partial t},
\]
where \( Q_a \) is the heat generation in real time \( t \); \( T_1 \) is the temperature at which \( Q_a \) is determined; \( C \) is the cement concentration [11]; \( r, t \) and \( \beta \) are the approximating constants for the description of the heat generation development. Hydration is determined by complex hydration mechanisms and the authors’ preferences. In terms of the heat and mass transfer in solid media, we use the hydration equation (2), which refers to the diffusion equation in Lothenbach’s model. Thermal activation of the early age behavior of Portland cement is described as
\[
\frac{\partial \varepsilon}{\partial t} = k(T) \frac{\partial T}{\partial t}.
\]
Assuming that the thermal conductivity coefficient is constant, we get \( \varepsilon = k(T - T_1) \), where \( T_1 \) is the initial laying temperature. The obtained relation can be used to detect the thermal stress from \( \sigma = k(T)f(E)\varepsilon \), where \( E \) is the Young modulus. The function \( f(E) \) regards a tensor coupling of strains and stresses. The formulated diffusion distribution of the heat flows, the temperature dependence of displacements and deformations, and the hydration intensity allow us to utilize Lothenbach’s model in the estimation of thermal stresses in the temperature gradient conditions and time-dependent stresses at different stages of cement curing.
3. Results and discussion
Let us consider the two-dimensional finite element model (FEM) presented in figure 1 for Portland cement curing during seven days. The water-cement ratio was assumed to be 0.40; the clinker minerals were given in table 1. Using Lothenbach’s model [1–3], we examined the hydration constant of several clinker minerals in considerable detail. The obtained results allowed for the weight percentage of hydration products of some of phases from the hydration constant equation (3) and also their effective content:

\[
\frac{\partial q(t)}{\partial t} = \sum_{i} b_i \left( K_{2i} \left( 1 - x(t) \right)^{2/3} \right. \cdot f \left( w / c \right) \cdot \exp \left( \frac{T_{ref} - T(t)}{RT_{ref}T(t)} \right) \cdot E_{ai},
\]

where \( b_i = m_i / M \), \( m_i \) is the weight of clinker minerals, \( M \) is the total weight, \( i \) is the number of minerals.

**Figure 1.** Two-dimensional FEM (a) and temperature distribution in the cement rod after 7-day curing (b). Laying temperature: 20 °C. Central part of the rod is in the concrete timber. Red horizontal (at 5 and 7 cm height) and vertical (at 8 and 35 cm length) lines indicate the applied von Mises stress. The colour temperature scale shows min and max values.

FEM calculations were used to obtain thermal stresses evaluated in the elastic region. According to the plane view in figure 1a, the 7×70 cm cement rod was placed in a concrete timber 2×70 cm in size. The right edge of the concrete timber was held rigidly; the heat exchange between the timber and environment was assumed to be absent. The temperature of the left and right edges of the rod was 65 and –20 °C, respectively. Initially, the laying temperature of hydrated cement (cement + water) was 20 °C. The numerical simulation of the temperature and von Mises stress distributions were performed at the following cement parameters: 2300 kg/m³ density, 1.8 V/(m-K) thermal conductivity, 880 J/(kg-K) specific heat capacity, 25·10³ Pa Young modulus, 10⁻⁶ K⁻¹ thermal expansion coefficient, 38 kJ/mol activation energy. The concrete timber is characterized by a 532 kg/m³ density, 1.8 V/(m-K) thermal conductivity, 2700 J/(kg-K) specific heat capacity, and 12.1 GPa Young modulus.
Figure 2. Two-dimensional von Mises stress distribution in Portland cement after different curing time: \( a \) – 0.037 day, \( b \) – 0.51 day, \( c \) – 1 day, \( d \) – 2 days, \( e \) – 4 days, \( f \) – 7 days. Laying temperature: 20 °C. The colour stress scale shows min and max values after 7 days.

The calculation results are shown in figures 1–3. Figure 1b shows the temperature distribution in Portland cement after 7 days of curing. The two-dimensional temperature distribution is determined by using the colour time scale. As can be seen from figures 2 and 3e, the temperature gradient causes the notable intensity of thermal flows inside and at the boundaries of the cement rod. With increasing curing time, the region of higher temperature grows. The operation of thermal sources and the temperature gradients promote the formation of thermal stresses. The results of the model analysis of the von Mises stress distribution given in figures 1a and 2, are presented in figure 3. Figure 2 shows the von Mises stress distribution in the cement rod at different curing time of 0.037, 0.5, 1, 2, 4 and 7 days. The stress distribution is determined by using the colour scale. In all cases, the von Mises stress distribution is non-monotonic. One can see an abrupt change in the stress distribution at the cement/timber interface and on the left and right edges of the rod. With increasing curing time, the region of the higher stress grows. The maximum von Mises stress is observed at the right edge of the cement rod. For more detailed analysis of the von Mises stress distribution, it is measured along the directions 1 and 2 (see figure 1a).

In figure 3, the stress distribution is measured along the horizontal lines at a height of 5 and 7 cm. These plots give stresses calculated at different curing time and measured in fractions of a day (12 hours). According to figure 3, the stresses are rather non-uniform. Figure 3a shows, that with increasing curing time, the stresses grow and reach the maximum at a ~10 cm distance, while the minimum is detected at a distance varying from 35 to 55 cm. In approaching to the cold edge of the rod, the stress increases and reaches the maximum at the cement/timber interface. In is important to note that in the negative temperature range hydration does not occur. The lowest stress is observed near the hot edge of the rod (~3–4 cm), which then significantly grows and reaches the maximum at the cement/timber interface. In figure 3c, d, one can see the von Mises stress distribution along the vertical lines 2 (see figure 1a). With increasing curing time, the von Mises stress also grows. The stress in the concrete timber is higher than in the cement rod. According to the numerical simulation, the strength gain for 7 days in the temperature gradient conditions proves the complex nature of the heat flow generation during the curing process. Heterogeneous temperature fields induced by the temperature gradient and thermal sources, change with time as well as the temperature distribution and the peak position. The temperature gradient ranging from 65 to -20 °C provides the shift of the stress maximum towards the hot edge of the rod. Negative temperatures promote the formation of zero (or close to zero) stresses in the cement rod.
Figure 3. Von Mises stress distribution in cement rod (figure 1а): a – along line 1 at 7 cm height, b – at 5 cm height, c – along line 2 at 8 cm length, d – at 35 cm length. Temperature distribution (d) along line 1 (7 cm height) is given for different curing time. Legend shows different time of curing.

During the curing process, the thermal stress level may be higher than the pore wall strength. The high gradient of thermal stresses remains within 7 days of curing. The most important role in cement curing mechanisms plays the interphase boundaries. The intensive chemical reactions in the cement
rod result in the development of thermal flows. The superposition of direct and reverse heat flows occurs at the interfaces. These heat flows enable high thermal stresses in the cement rod, which either grow monotonically up to the highest values at the interfaces or abruptly grow in the concrete timber (see Fig. 3c, d). At a distance between 55 and 70 cm of the rod, the negative flow superposition leads to a high level of thermal stresses, which depend on the curing time. It should be noted that maximum stresses at the hot edge are lower than at the cold edge of the rod. At temperatures below 0 °C, the negative heat flows at the interphase boundaries also generate stresses higher than the maximum stresses in the cement rod. This effect is conditioned by the superposition of the direct and reverse heat flows produced by only the external temperature gradients. Hydration mechanisms of curing do not work in the distance range from 55 to 70 cm.

4. Conclusions
The numerical simulation of Portland cement curing for 7 days in the temperature gradient conditions showed the complex nature of the temperature and von Mises stress distribution. Non-monotonic stress distribution along the cement rod significantly depended on the curing time, temperature gradients, and thermal sources. In the temperature gradient conditions, the von Mises stress maximum, which exceeded the stress minimum by 2 or 2.5 times, shifted toward positive temperatures of the cement rod. The temperature gradients promoted the extreme values of stresses localized in the cement rod within the distance of 0–60 cm due to the superposition of direct and reverse thermal flows. It was found that the heat flow distribution caused by exothermic reactions were also affected by the concrete timber. The reverse heat flows formed at the rod edges and the heat flow superposition determined the high thermal stresses, which could go beyond the elastic regions of the cement rod. Negative temperatures at the rod edges provided the formation of critical stresses in the cement rod due to superposition of direct and reverse thermal flows generated by the negative temperature gradient. At the rod edge with negative temperature, the stress exceeded the pore wall yield point in the cement rod. The level of stresses was also affected by the concrete timber.

5. References
[1] Lothenbach B, Matschei T, Möschner G and Glasser F P 2008 Cem. Concr. Res. 38 1–18
[2] Lothenbach B and Winnefeld F 2006 Cem. Concr. Res. 36 209–226
[3] Matschei T, Lothenbach B and Glasser F P 2008 Cem. Concr. Res. 37 1379–1410
[4] Lothenbach B, Le Saout G, Ben Haha M, Figi R and Wieland E 2012 Cem. Concr. Res. 42 410–423
[5] Pelletier-Chaignat L, Winnefeld F, Lothenbach B and Müller C J 2012 Constr. Build. Mater. 26 619–627
[6] Pelletier-Chaignat L, Winnefeld F, Lothenbach B, Le Saout G, Müller C J and Famy C 2011 Constr. Build. Mater. 26 551–561
[7] Parrot L J and Killoh D C 1984 Proc. Br. Ceram. Soc. 35 41–53
[8] Abzaev Y, Gnyrya A, Korobkov S, Dudov D, Mihailov D and Vodnev B 2019 EPJ Web Conf. 221 01001
[9] Bentz D P 1995 A Three-Dimensional Cement Hydration and Microstructures Program. I. Hydration Rate, Heat of Hydration and Chemical Shrinkage (Maryland: NISTIR 5756) pp 1–47
[10] Neville A 2012 Properties of Concrete 5th edition (Harlow: Pearson Education)
[11] Cervera M, Oliver J and Prato T 1999 J. Eng. Mech. 125 1018–1027
[12] Cervera M, Oliver J and Prato T 1999 J. Eng. Mech. 125 1028–1039
[13] Ulm F J and Coussy O J. 1996 Eng. Mech. 122 1123–1132
[14] Gasch T, Sjölander A, Malm R and Ansell A 2016 Proc. 9th Int. Conf. on Fracture Mechanics of Concrete and Concrete Structures (Berkeley, USA)
[15] Powers T C, 1947 Proc. Highw. Res. Bd. 27 178–188
[16] Bazant Z P, Cusatis G and Cedolin L 2004 J. Eng. Mech. 130 691–699
[17] Khan A A, Cook W D and Mitchell D 1995 ACI Mater. J. 92 617–624
[18] van Breugel K 1991 *Simulation of Hydration and Formation of Structure in Hardening Cement-Based Materials*, PhD Thesis (Delft University Press, The Netherlands)

[19] Caggiano A, Pepe M, Koender E A B, Martinelli E and Etse G 2012 *Mecânica Computacional* **XXXI**, 1893–1907

[20] Tennis P D and Jennings H M 2000 *Cem. Concr. Res*. **30** 855–863

**Acknowledgement**

This work was financially supported by Grant №18-08-01025 from the Russian Foundation for Basic Research.