Modeling Heat and Moisture Transport During Hydration of Cement-Based Materials in Semi-Adiabatic Conditions

E. Hernandez-Bautista[1,2], D. P. Bentz[1], S. Sandoval-Torres[2], P. F de J. Cano-Barrita[2]

[1] National Institute of Standards and Technology, Gaithersburg, MD, USA.
[2] Instituto Politécnico Nacional/CIIDIR Unidad Oaxaca, Hornos, Oaxaca, México
*Corresponding author: Oaxaca de Juarez, Oaxaca, ehernandezb0800@alumno.ipn.mx

Abstract: The process of accelerated curing of pre-cast concrete consists in increasing the temperature within a saturated water vapor atmosphere during several hours. In this process, the cement hydration has a significant importance in the thermal behavior of concrete, since it has an effect on both the mechanical and durability properties. A Multiphysics model that describes hydration and heat and mass transport in cement-based materials was developed. The hydration reactions are described by a maturity function that uses the equivalent time concept, thereby describing the change in the degree of hydration based on the time-temperature history in the form of Domain Ordinary Differential Equations. These equations are coupled to a heat balance, using the COMSOL Heat Transfer module. Using the PDE general form, we solved the moisture content conservation equation. The numerical results were compared with the experimental temperatures obtained directly by semi-adiabatic temperature measurements. The numerical results show a good agreement

Keywords: Portland cement, maturity, hydration degree, heat transfer, mass transfer, semi-adiabatic condition

1. Introduction

Steam curing of hydraulic concrete in the precast industry has the advantage of accelerating the hydration reactions of cement. Consequently, the material develops compressive strength and reduces its permeability in hours, compared to standard curing under normal environmental conditions, where the hydration reactions require several days or even months to achieve an adequate degree of hydration [1].

The aim of this work is to model the moisture and heat transport in a semi–adiabatic condition in cement pastes and mortars, by coupling the evolution of hydration reactions

2. Use of COMSOL Multiphysics

In order to simulate a semi-adiabatic configuration, we used the experimental isothermal calorimetric data. This data was used to establish the input parameters. The geometry of the calorimeter and the properties of the materials used in the semi-adiabatic test were implemented in Comsol Multiphysics 4.4. A 2D axisymmetric geometry is shown in Figure 1. The main domain is framed in cylindrical coordinates. The geometry consists of four subdomains (i) , which represent 1) cement-based material 2) LDPE container; 3) the air volume existing between the top surface of the cement and the container lid; 4) insulation wall.
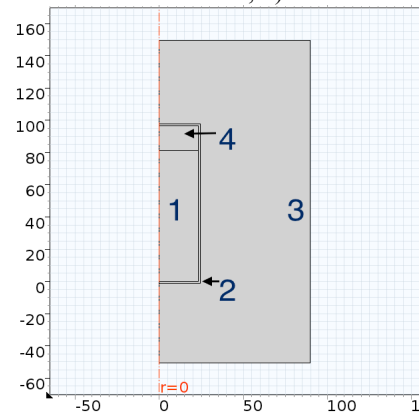
Figure 1. Two-dimensional geometry with four subdomains in millimeters.

2.1 Hydration in the Domain ordinary differential equations (DODE)

The maturity method is used to account for the effect of temperature and time on the formation of hydration products, since the temperature has a large effect on the concrete setting times and strength development [2].

The equivalent age and the maturity equations were implemented in Comsol Multiphysics in the form of ordinary differential equations. Within the domain of the mortar (subdomain 1) the hydration reactions occur. Equation (1) represents the equivalent age written in the form of a DODE with an initial condition equal to 0. This equation describes the changes of temperature during hydration. For every change

in temperature, we have a new equivalent age (time).

$$\frac{dt_e}{dt} = \exp\left[\frac{E}{R}\left(\frac{1}{T_r} - \frac{1}{T}\right)\right] \quad t = 0 \ \ then \ \ t_e = 0 \quad (1)$$

where t_e is the equivalent time or equivalent age at the reference curing temperature, dt is the time interval (h), T_c is the average concrete temperature during the interval dt (K), T_r is the constant reference temperature (K), E the activation energy (J/mol) and R is the universal gas constant (8.314 J/(mol·K)).
The maturity equation was derived with respect to t_e and was implemented in Comsol Multiphysics as Equation (2), which shows a coupling between the equivalent time and the degree of hydration [5].

$$\frac{d\alpha}{dt} = \exp\left[\frac{E}{R}\left(\frac{1}{T_r} - \frac{1}{T}\right)\right] \cdot \frac{\alpha_u \beta}{t_e}\left(\frac{\tau}{t_e}\right)^{\beta} \exp\left[-\left(\frac{\tau}{t_e}\right)^{\beta}\right] t = 0 \ \ then \ \ \alpha = 0 \quad (2)$$

where α (t_e) is the degree of hydration at equivalent age t_e, τ is the hydration time (h), β is the hydration shape parameter.

2.2 Energy conservation
The energy conservation equation was applied to all subdomains in the model in order to obtain the total heat generated by the chemical reactions. We consider the loss of heat to the container and subsequently to the thermal insulation wall. Equation (3) represents the energy conservation in the subdomain i.

$$\rho_i Cp_i \frac{\partial T}{\partial t} = \nabla \cdot \left(k_i \nabla T\right) + Q_i \quad (3)$$

Where i is the type of material. In the cement-based material, the specific Cp heat and thermal conductivity k are obtained from Table (1) for a cement paste with water-to-cement ratio (w/c) = 0.30.
For the domain of air, the values of thermal conductivity, heat capacity and density were taken from the Comsol library. All these values depend on the temperature of the domain. The properties of de LDPE were obtained from [6].
The heat generation rate Q corresponds to the exothermic reactions in the subdomain 1. Q was described as a derived function of the degree of hydration with respect to time multiplied by the final heat of hydration, which was obtained from the isothermal measurements.

The cumulative heat release was obtained by multiplying the degree of hydration by the final heat of hydration [3].
The ultimate degree of hydration Hu indicates the ultimate heat release expected when all of the cement is able to hydrate, based on its known chemical (Bogue) composition.
The value of H_u (Table 1) was used in the model in order to compute the heat generation rate. Then, we have:

$$\frac{dH}{dt_e} = \frac{H_u \alpha_u \beta}{t_e}\left(\frac{\tau}{t_e}\right)^{\beta} \exp\left[-\left(\frac{\tau}{t_e}\right)^{\beta}\right] \quad (4)$$

The generation source was also considered in the energy conservation Equation (4), with the source term being expressed in units of W/m^2. The source term is equal to zero for the subdomains in the air phase, LDPE and the insulation wall.

2.3 Mass conservation
The moisture conservation balance was applied to the subdomain of the cement-based material. This balance is described by 2 equations that include the transport of vapor (h) (Equation 4) and transport of liquid water (Equation 5) that is the sum of free water and vapor. In this study, the bound water content was not considered.

$$\frac{\partial h}{\partial t} = \frac{\partial h}{\partial x}\left[D_v(h)\frac{\partial h}{\partial x}\right] \quad (5)$$

$$\rho_s \frac{\partial w}{\partial h}\frac{\partial h}{\partial t} = \frac{\partial h}{\partial x}\left[\rho_s \cdot D_l(h)\frac{\partial w}{\partial h}\frac{\partial h}{\partial x} + D_v(h)\frac{\partial h}{\partial x}\right] + S \quad (6)$$

The diffusion coefficients of $\mathbf{D}_l$ (liquid water) and $\mathbf{D}_v$ (vapor) were taken from Villmann et al. (2014) [4] and depend on the relative humidity.
Another important term obtained from the equations of the maturity model is the sink of free water consumed by the hydration reactions, which will be considered in the equation of the moisture conservation, Equation (5).

$$S = -\rho_s w_i \frac{d\alpha}{dt} \quad (7)$$

where ρ_s is the solid density and w_i is the initial moisture content obtained from the mixture design. The sink of water in the material is computed in units of kg/(m^2·s)

Table 1: Cement paste properties (w/c = 0.30)

Parameter	Value	Unit
Thermal conductivity	2.6	W/(m·K)
Heat capacity	1520	J/(kg·K)
Tau	11.4823	(1)
Betha	1.3051	(h)
Ultimate degree of hydration	0.549	(1)
Ultimate heat of hydration	4.79	(J/kg)
Activation energy	32000	(J/mol)
Diffusion coefficient of the liquid water	6. x10^{-9}	(m/s^2)

2.4 Boundary and initial conditions

One of the assumptions in the model is that there exists a perfect contact between the materials; therefore, the applied boundary conditions are a continuous boundary in the cement-air, cement-LDPE and LDPE-Insulation boundaries.

$$\mathbf{n} \cdot \left[(k\nabla T)_{\Omega 1} - (k\nabla T)_{\Omega 2} \right] = 0 \quad (8)$$

At the surface of the insulation wall we have a convective boundary condition that was described by Newton's law of cooling (Eq. 9).

$$-\mathbf{n} \cdot (-k\nabla T) = q_0 = h \cdot (T_{ext} - T) \quad (9)$$

where h is the convective heat transfer coefficient with a value of 15 W/(m2 ·K) [7]. of the initial conditions are 23 ºC and 23.5 ºC for the sample and the surrounding respectively.

2.5 Mesh geometry and solution

The mesh geometry consists of 1921 domain elements and 241 boundary elements. The number of degrees of freedom was 10596. The system of PDEs was solved with a time step of 1 min from 0.1 to 120 h, using a relative tolerance of 0.01.

3. Results: Simulation of hydration in cement pastes in semi-adiabatic conditions

The temperature evolution, the degree of hydration, and the moisture content transport,

were simulated using Comsol Multiphysics 4.4. The inputs of the model are: the parameters calculated from the isothermal calorimetry including ultimate heat of hydration and parameters of the maturity model (Table 1).
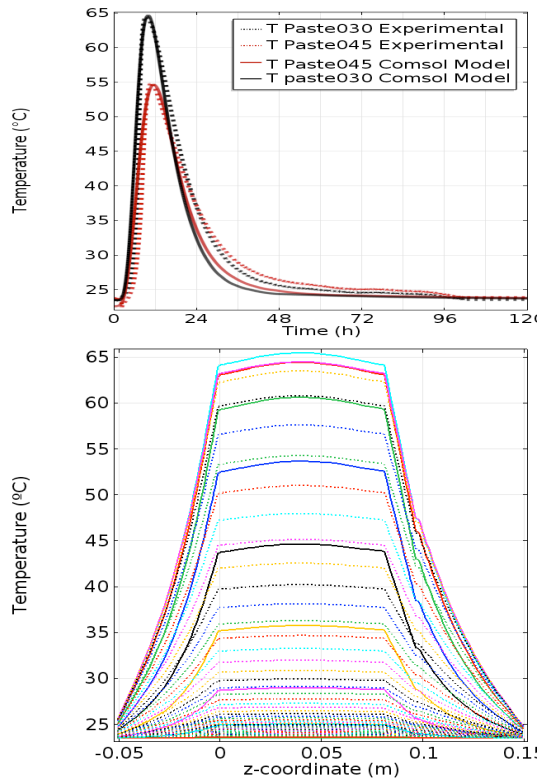
The distribution of temperature is shown in 3D view in Figure 2, using the axisymmetric model in cylindrical coordinates (r, θ and z). The experimental temperature in the cylinder in semi-adiabatic conditions shows two stages of heating and cooling. Figure 2 shows the 3D spatial distribution of temperature in all domains, the maximum temperature reached, and the temperature at one time during the cooling stage.
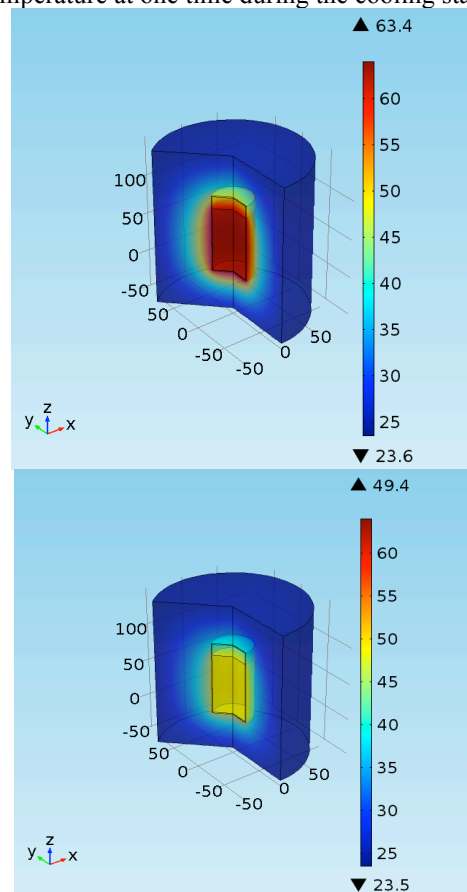
Figure 2. Temperature distribution (ºC) in the simulated semi adiabatic calorimetric test (top) at 12 h and (bottom) at 16 h.

Figure 3 (top) shows the comparison of temperature evolution between the cylinders in the semi-adiabatic calorimetry experiments (dotted line) and the result of the simulation using the developed model (solid line). Two different w/c in cement pastes were simulated,
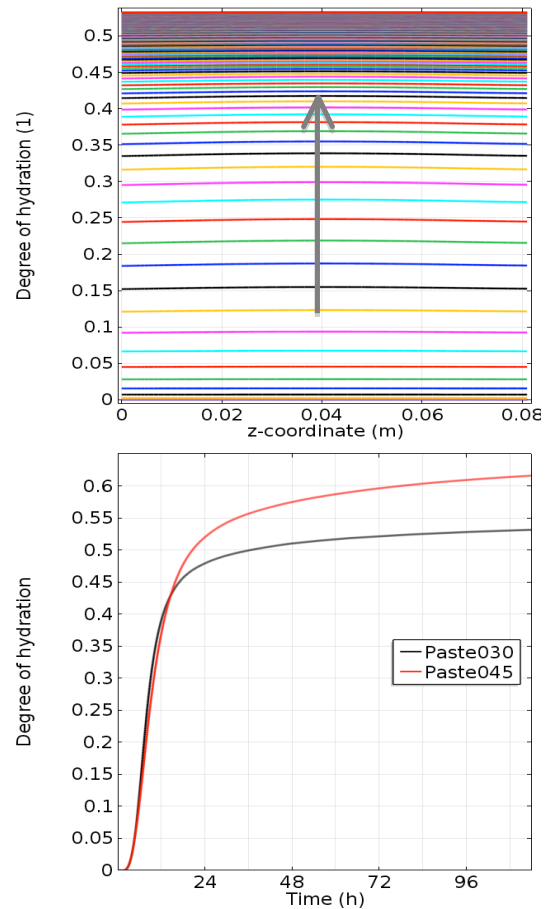
0.30 and 0.45. The simulations predict maximum temperatures of 63 ºC and 55 ºC at 12 h for cement pastes with w/c ratios of 0.30 and 0.45, respectively. The cooling stage after approximately two days fit well in the case of 0.30, but shows an over prediction in the case of 0.45. Some heat could have dissipated from water evaporation, which was not taken into account.

The model is also able to compute the degree of hydration in the subdomain of the cement using the maturity function. Figure 4 (top), shows the variation of the degree of hydration in the domain of the paste (w/c=0.30), this variation is lineal in the z direction because the variation of the temperature directly affects the evolution of the degree of hydration. Figure 4 (down) shows the evolution of the average degree of hydration in the paste and its evolution in time, for the two different w/c.

Figure 3. Comparison of the evolution of measured temperature in the semi-adiabatic calorimetric test with the simulation (top) and spatial distribution of temperature in z direction simulated in *w/c*=0.30 paste every 30 min (bottom)

Figure 3 (top) displays the spatial distribution of temperature simulated in the paste w/c=0.30 in the z direction (cylindrical coordinates, of the height of the LDPE container from 0 to 82 mm. The figure also includes the variation of the temperature in the insulation wall. The solid lines describe the temperature during the heating stage (before 12 h) and the dotted lines correspond to the cooling stage (after 12 h).

Figure 4 Spatial distribution of degree of hydration in z direction simulated in the paste *w/c*=0.30 every 30 min (top) and average for *w/c*=0.30 and 0.45 (bottom).

In Figure 5, the distribution of moisture in the paste w/c=0.30 is shown. Figure 5a shows the spatial distribution of moisture in the paste every 30 min. During the first 12 h the loss of moisture depends on the consumption of water by the chemical reactions and the loss of water at the top surface, while after 12 h it depends mainly on the loss of mass by evaporation at the surface.
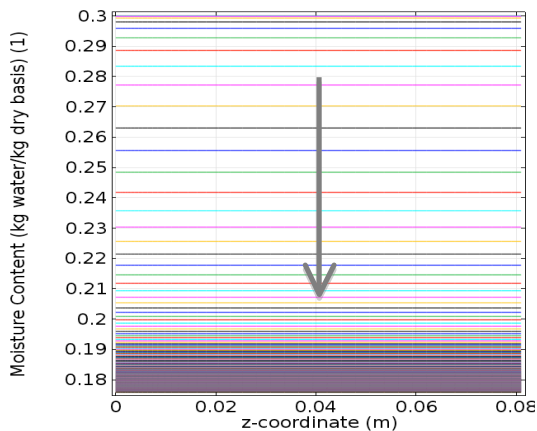
Figure 5 Spatial distribution of moisture in z direction simulated in the paste *w/*c=0.30 every 30 min.

Figure 5 shows the average moisture content in the complete subdomain of the cement paste for w/c = 0.30. The moisture content decreases until the maximum degree of hydration of 0.55 is reached at 23 ºC. The loss of free moisture in the paste is mainly due to the hydration reactions as opposed to evaporation at the surface for the current experimental setup.

4. Conclusions

Our simulations describe the heat conduction, degree of hydration evolutions and the moisture content transport in a cement material.
The model describes the hydration as a function of temperature using the equivalent age concept and the maturity equations in order to describe the hydration reactions.
The variation of the temperature and moisture content is described using total conservation equations for heat and moisture.
The model was used to simulate the temperature evolution in the semi-adiabatic calorimetric test, and it was compared with the experimental data and the simulated results.
The model predicts the degree of hydration and the moisture evolution in the subdomain of the paste.

Future work

The next step of the work will be to extend the simulations to the semi-adiabatic conditions used for curing mortars. Furthermore, in the case of the moisture equation, the variation of the

relative humidity in the pores due to chemical shrinkage.

5. References

1. Kosmatka, S.H., Kerkhoff, B. & Panarese, W.C. Design and Control Design and Control of Concrete Mixtures Fourteenth. *P. C. Association, ed., Portland cement Association*. (2003)
2. Freiesleben Hansen, P Pedersen, J., Maturity Computer for Controlled Curing and Hardening of Concrete. *Nordisk Betong*, 19–34.(1977)
3. Bentz, D.P. Transient plane source measurements of the thermal properties of hydrating cement pastes. *Materials and Structures*, 40, 1073–1080. (2007)
4. Villmann, B. et al., Time-dependent Moisture Distribution in Drying Cement Mortars. Results of Neutron Radiography and Inverse Analysis of Drying Tests Determination of Moisture Transport Parameters and Moisture Profiles by Inverse Analysis. *Cement and Concrete Research*, 20(1), pp.49–62.(2014.)
5. Chini, a. R., Effect of elevated curing temperatures on the strength and durability of concrete. *Materials and Structures*, 38, 673–679. (2005)
6. Mark, J.E., Physical Properties of Polymers Handbook Mark, *Springer ScienceþBusiness Media*. (1990)
7. Smilauer, V. & Krejci, T., Multiscale model for temperature distribution in hydrating concrete. *International Journal for Multiscale Computational Engineering*, 7(2), (2009)

6. Acknowledgements