

Verification, Validation, and Variability of Virtual Standards

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As the potential of computer modeling of hydration and microstructure development of cement-based materials approaches realization, the development of *virtual* standard test methods becomes a viable possibility. In creating these virtual standards, just as with the development of any physical standard test method, verification, validation (calibration), and variability must all be considered. These three issues will be discussed in reference to the ongoing development of a prototype virtual test method for the heat of hydration of ordinary portland cement within ASTM subcommittee C 01.26. The virtual test method employs the CEMHYD3D v3.0 cement hydration and microstructure development model and an early-age physical measurement of chemical shrinkage (via the ASTM C 1608 test method), to predict the 7-day and 28-day heat of hydration values in comparison to those measured via the ASTM C 186 Heat of Hydration test method in recent Cement and Concrete Reference Laboratory cement proficiency sample programs.

1. Introduction

Test methods for the physical properties of cement-based materials are one central component of the longstanding and successful application of these materials in building and construction. Physical test methods exist for the characterization of the starting materials (fineness, chemical composition), their properties in the “fresh” state (setting time by Vicat needle, air content, normal consistency), their properties in the hardened state (compressive strength, sorptivity), and their durability (freeze/thaw testing, sulfate attack). Especially in the latter two cases, the aging times of the specimens prior to or during testing can be quite long (typically 28 d for compressive strength or heat of hydration, 1 year or longer for some durability test exposures). One impetus for the development of virtual test methods is to achieve a reduction in testing time by predicting the longer term performance from a virtual test method, alone or in concert with an early age physical test method [1]. Virtual test methods should also result in a reduction in material and labor costs, as the amount of physical testing could be optimized and focused in problematic or promising arenas as opposed to the mundane but necessary day-to-day quality control type testing. Computer models that predict physical properties such as heat release, hydration rates, chemical shrinkage, setting time, compressive strength, and ionic diffusion coefficients have been developed and

integrated into Internet-accessible packages, such as the Virtual Cement and Concrete Testing Laboratory (VCCTL) [1-3]. As these computer models are transformed into virtual standards, appropriate attention must be paid to their verification, validation, and variability [4-7].

Simply put, verification and validation refer to “building the model right” and “building the right model”, respectively [4, 5]. In more formal terms, verification is defined as “*the process of determining that a model implementation accurately represents the developer’s conceptual description of the model and the solution to the model*” [6]. Validation is defined as “*the process of determining the degree to which a model is an accurate representation of the real world from the perspective of the intended uses of the model*” [6]. A concept related to validation is that of calibration, which is defined as “*the process of adjusting numerical or physical modeling parameters in the computational model for the purpose of improving agreement with experimental data*” [6].

Mapping these concepts into the world of physical test method development, one could define verification as “building the physical test method right” and validation as “building the right physical test method.” A concrete example can be given by considering the ASTM C 39 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens [8]. In this case, verification would be concerned with assuring that the developed test method accurately assesses the compressive strength of a concrete cylinder in a repeatable manner. Specimen end conditions (grinding, capping, etc.), specimen casting and pre-conditioning, and specimen loading rates must all be specified along with allowable tolerances to assure that the test method has been “built right”. Conversely, validation would be concerned with whether measurement of compressive strength of concrete cylinders is an appropriate measure of the quality of field concrete. Measurement of compressive strength is an interesting example in that both verification and validation have been re-examined within the past 15 years in light of ongoing developments in high strength and high performance concretes. For example, Carino et al. have considered the effects of a variety of testing parameters on the measured strengths of high-strength concretes [9-11], part of the verification process. Concurrently, the appropriateness of using compressive strength to characterize a high performance concrete mixture versus using a transport property or durability test that may be more relevant to long term concrete performance, such as rapid chloride permeability or freeze/thaw durability, has also been debated [12] as part of the validation process.

Extending the above concepts to a virtual standard that is based on an underlying computer model brings us full circle back to the original definitions of verification and validation, “building the (computer) model

right” and “building the right (computer) model”. Verification is now the process of determining whether the computer model correctly implements the underlying conceptual model on which it is based. Thus, one of the major steps in verification is commonly the “debugging” of the computer software. Validation is then the process of determining whether the implemented and verified computer model accurately represents the real world, at least for its intended uses. When a corresponding accepted physical test method already exists, validation may simply consist of validating that the virtual test method produces computational results that are statistically indistinguishable from the measured results of the physical test [7]. Validation may proceed to calibration when one or more model parameters are adjusted to obtain better agreement between the computational and the measured results. In this paper, the development of a prototype virtual test method for the heat of hydration of portland cement will be presented, with regard being given to verification, validation, and variability.

2. Experimental and Modeling

2.1 Verification

In CEMHYD3D v3.0, the conceptual model for heat of hydration is that the cumulative heat of hydration can be obtained at any age by multiplying the mass of each phase that has reacted by its enthalpy of hydration value, summing the results, and dividing by the total mass of cementitious material. The enthalpies of hydration employed in the model, as taken from the literature [13-15], are summarized in Table 1. For this part of the computer model, verification tasks have included verifying that the correct coefficients from Table 1 are used with the correct phases in the computer program and that the executable software does indeed produce the “correct” heat of hydration values according to the conceptual model for a cement of known composition.

Table 1. Enthalpy of Hydration for Major Portland Cement Phases [13-15]

Phase	Enthalpy (kJ/kg phase)
C ₃ S	517
C ₂ S	262
C ₃ A	908, 1672, 1144 ^A
C ₄ AF	418, 725 ^B
Anhydrite (to gypsum)	187
Hemihydrate (to gypsum)	132

^A For C₃A hydration, values are for conversion to C₃AH₆, ettringite, and monosulfate (Afm) phase, respectively.

^B For C₄AF hydration, values are for conversion to C₃AH₆ and ettringite, respectively.

2.2 Validation

For validating the virtual test method, experimental data previously generated in the Cement and Concrete Reference Laboratory (CCRL) proficiency sample program has been employed [16]. Specifically, five different CCRL cements issued between 1995 and 2004 have been examined. The properties of these cements are summarized in the cements database included in the VCCTL [2]. Their phase composition, as provided in Table 2, has been determined using a scanning electron microscopy (SEM)/X-ray imaging technique [17]. For cements 141 and 152, estimates of the proportions of the various calcium sulfate components (gypsum, hemihydrate, and anhydrite) have been obtained from X-ray diffraction analysis. In addition, the particle size distribution (PSD) of each cement has been measured using a laser diffraction technique.

Table 2. Composition of CCRL proficiency sample program portland cements (volume fractions).

Phase	CCRL 115	CCRL 116	CCRL 135	CCRL 141	CCRL 152
C₃S	0.596	0.627	0.634	0.632	0.690
C₂S	0.218	0.207	0.162	0.106	0.088
C₃A	0.031	0.067	0.066	0.115	0.123
C₄AF	0.095	0.034	0.078	0.073	0.038
Gypsum	0.060	0.065	0.060	0.026	0.027
Hemihydrate	Not meas.	Not meas.	Not meas.	0.048	0.031
Anhydrite	Not meas.	Not meas.	Not meas.	0.000	0.003

Using the five cements shown in Table 2, the following prototype virtual test methodology has been examined:

- 1) obtain a physical sample of the cement of interest and characterize it with respect to PSD and volumetric phase composition based on SEM/X-ray image analysis or X-ray diffraction (standards for the PSD and phase characterization methods are currently being pursued in the ASTM C01.25 and ASTM C01.23 subcommittees, respectively),
- 2) prepare a $w/c=0.4$ (23 °C) cement paste specimen and measure its chemical shrinkage according to the ASTM C 1608 test method [18], during at least the first 8 h of hydration; use the measured response to calibrate the kinetics factor, β , that connects to time in the CEMHYD3D v3.0 computer model [19] for this cement,
- 3) using the same calibrated kinetics factor, conduct a virtual heat of hydration experiment ($w/c=0.4$, sealed hydration at 23 °C) with CEMHYD3D v3.0 to obtain the 7 d and 28 d (and other) heat of hydration

values for comparison to the experimentally measured values from the ASTM C 186 test method [20],

4) optionally, conduct adiabatic hydrations, etc. to estimate the adiabatic temperature rise of concrete mixtures of interest produced with this cement, (beyond the scope of this paper, but illustrated in a previous publication [21]).

All virtual tests (chemical shrinkage and heat of hydration) were conducted using the freely available CEMHYD3D version 3.0 software for modeling cement hydration and microstructure development [19]. The CEMHYD3D simulations were conducted under two sets of starting conditions. In the first case, the simulations were conducted using the complete available characterization of the cements, including their phase composition, phase surface area fractions, and phase correlation functions [2, 17, 19, 22], as determined from the SEM/X-ray imaging analysis. In the second case, it was assumed that only their volumetric phase compositions were available, as would be the case if solely the more widely available X-ray diffraction were used for cement phase characterization. In the second case, for each of the five cements, it was assumed that each individual phase's surface area fraction was equivalent to its volume fraction and the correlation functions from a previously characterized CCRL cement (cement 133) were used as being characteristic of each cement. The total alkali contents of the cements were taken directly from the CCRL summary reports. For three of the cements (see Table 3), the readily soluble alkalis (sodium and potassium) were measured in the NIST laboratory for 1 h old filtered pore solutions; for the other two, the readily soluble alkalis were assumed to be 80 % of their respective total alkali values [13]. The measured and assumed activation energies for the hydration reactions for each cement are also provided in Table 3.

In general, the simulation of the chemical shrinkage test ($w/c=0.4$, $T=20$ °C to 25 °C, saturated curing) was executed with a default kinetics factor of 0.00035 [19]. This parameter was then adjusted using a spreadsheet to provide the best agreement between the model and experimentally measured chemical shrinkages in the 8 h to 10 h time range, as will be demonstrated in the Results section. The adjusted kinetics factors obtained in this manner are also provided in Table 3. This adjusted kinetics factor value was then used for the subsequent simulation of hydration under sealed conditions for the heat of hydration virtual test method ($w/c=0.4$ at 23 °C). In the case of CCRL cement 152, three separate simulations with independently generated random starting microstructures were executed to provide some indication of the variability of the prototype virtual test method when executed as outlined above.

Table 3. Parameters used in the CEMHYD3D v3.0 modeling of the hydration reactions of the five different CCRL cements.

CCRL Cement	CEMHYD3D (complete characterization) kinetics factor	CEMHYD3D (volume only) kinetics factor	Activation Energy (kJ/mol)	Readily-soluble (1 h) alkalis
115	0.00022	0.00023	41.3 [*]	Assumed as 80 %
116	0.00043	0.00050	40.0 [*]	Assumed as 80 %
135	0.00035	0.00035	40.0 ⁺	Measured
141	0.00035	0.00035	40.0 ⁺	Measured
152	0.00027	0.00027	45.5 [*]	Measured
152 rep1	0.00030	0.00032	45.5	Measured
152 rep2	0.00030	0.00030	45.5	Measured

^{*}Activation energy measured at NIST by isothermal hydration at 2 or more temperatures [22, 23].

⁺Activation energy assumed to be 40.0 kJ/mol based on ASTM C 1074 [24].

3. Results and Discussion

3.1 Validation (Calibration)

Fourteen sets of simulations were conducted to validate the use of the prototype virtual test method for predicting 7 d and 28 d heat of hydration. As stated above, the chemical shrinkage simulations were compared to experimental results in order to calibrate the kinetics factor of the CEMHYD3D model. The obtained heat of hydration results in comparison to those measured in the CCRL proficiency sample testing program are summarized in Table 4, while representative curves for the experimental and model chemical shrinkage and heat of hydration are provided in Figures 1 and 2, respectively. In this preliminary study, the agreement between calibrated model data and the measured values is quite reasonable, both for the chemical shrinkage measured according to ASTM C 1608 and the heat of hydration measured according to ASTM C 186, even for the cases where only the measured phase volume fractions were used as input for the simulations. It can be observed that better predictions are obtained when the readily-soluble (1 h) alkalis are directly measured (cements 135, 141, and 152) than when they are assumed to be 80 % of the total alkalis (cements 115 and 116). The worst case agreement between virtual and measured C 186 heat of hydration is found for the 28 d prediction for cement 116, where the virtual values based on a complete characterization or a “volume only” characterization differ from the measured average value by 1.11 and 1.33 (CCRL measured) standard

Table 4. CCRL measured and CEMHYD3D predicted heats of hydration at 7 d and 28 d for five different cements from the CCRL proficiency sample program.

CCRL cement	Age (d) (# of labs)	CCRL C186 heat of hyd. (J/g)	CCRL std. dev. (J/g)	CEMHYD3D (complete) heat of hyd. (J/g)	 Model-Meas. / (Meas. dev.)	CEMHYD3D (volume only) heat of hyd. (J/g)	 Model-Meas. / (Meas. dev.)
115	7 (27)	310.9	27.6	305.3	0.20	303.8	0.26
115	28 (16)	368.6	21.8	346.3	1.02	345.0	1.08
116	7 (27)	359.8	25.9	339.6	0.78	331.3	1.1
116	28 (16)	402.1	17.2	383.0	1.11	379.3	1.33
135	7 (22)	326.4	21.8	327.4	0.05	327.4	0.05
135	28 (15)	360.2	19.2	375.0	0.77	371.6	0.59
141	7 (18)	351.1	30.96	344.2	0.22	344.7	0.21
141	28 (11)	380.7	36.4	399.6	0.52	398.4	0.49
152	7 (22)	362.8	30.96	373.6	0.35	371.5	0.28
152	28 (18)	415	23.85	419.0	0.17	416.9	0.08
152-1	7 (22)	362.8	30.96	374.2	0.37	370.8	0.26
152-1	28 (18)	415	23.85	416.6	0.07	415.5	0.02
152-2	7 (22)	362.8	30.96	369.2	0.21	371.6	0.28
152-2	28 (18)	415	23.85	416.4	0.06	416.0	0.04

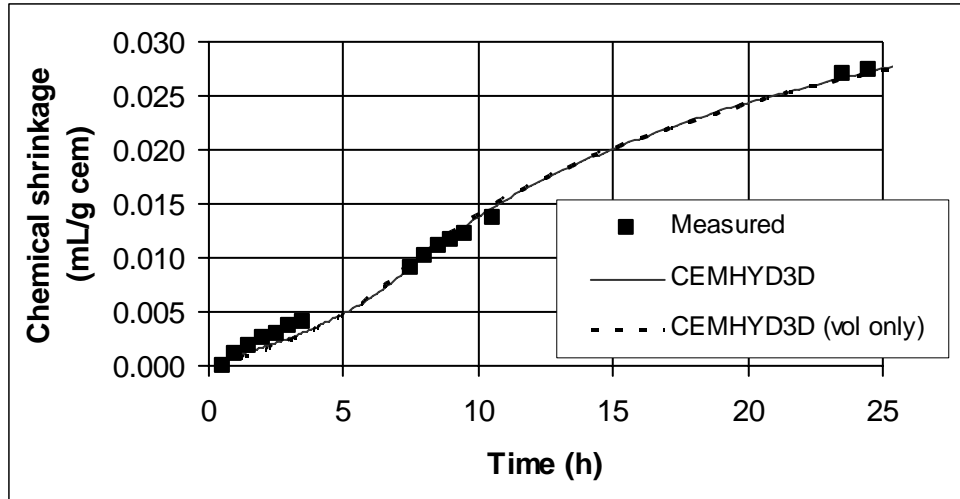


Figure 1. Measured and CEMHYD3D predicted chemical shrinkage for CCRL cement 141 ($w/c=0.4$, $20\text{ }^{\circ}\text{C}$).

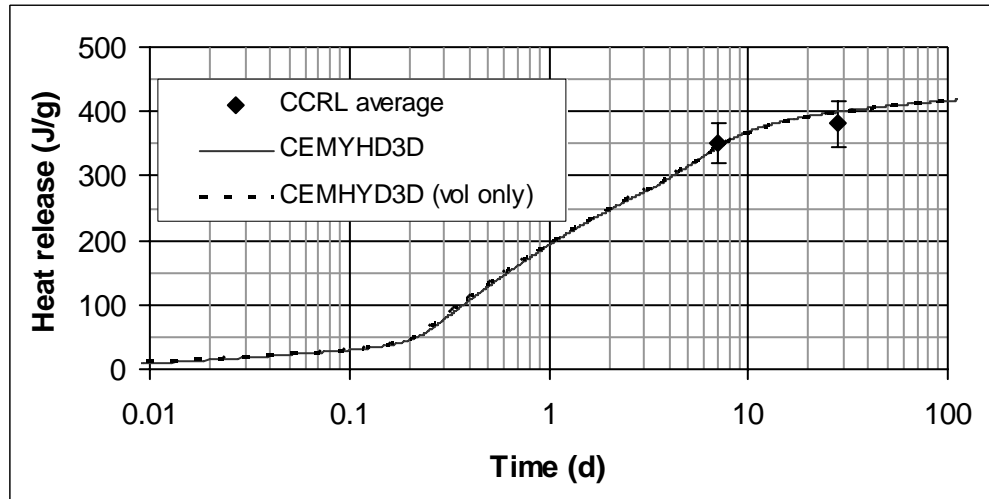


Figure 2. Measured and CEMHYD3D predicted heat of hydration for CCRL cement 141 ($w/c=0.4$, $23\text{ }^{\circ}\text{C}$). Error bars indicate one standard deviation as determined in the CCRL testing program.

deviations, respectively. In a majority of the cases, model predictions are within one half of a standard deviation of the average value measured in the CCRL proficiency sample testing program.

3.2 Variability

In this preliminary study, one aspect of the variability of the virtual test method has been examined by conducting replicate simulations based on independently generated random starting microstructures. For cement 152, three independent starting microstructures were generated by simply changing the random number seeds that are utilized for random particle

placement, phase distribution, and hydration. Each replicate starting microstructure was submitted to the simulation of chemical shrinkage to calibrate its kinetics factor and then to the simulation of heat of hydration. The results obtained for the first case, where the complete characterization of the cement was employed, are provided in Figures 3 and 4. By calibrating the kinetics factor for each starting microstructure (Table 3), the obtained curves for predicted chemical shrinkage and heat release are quite similar amongst the three replicates. Three different random starting microstructures were also generated for the case where only the phase volume composition of the cement was provided. In each of these two cases, for the three replicates evaluated, the achieved coefficients of variation in the predicted 7 d and 28 d heat of hydration were well below 1 %, as indicated in Table 4.

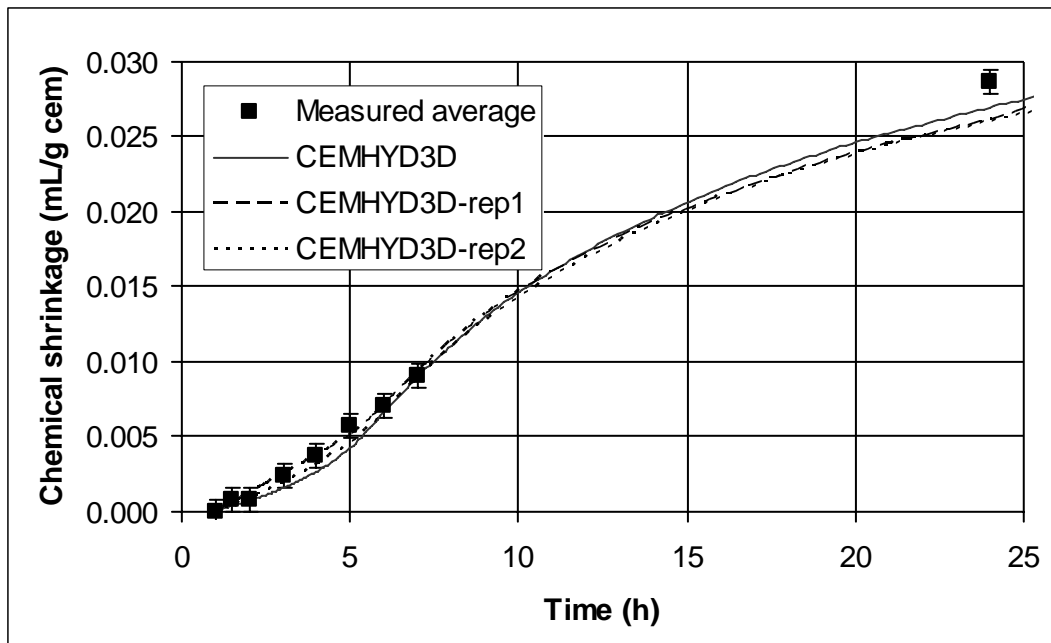


Figure 3. Measured and CEMHYD3D predicted chemical shrinkage for CCRL cement 152 ($w/c=0.4$, $23\text{ }^{\circ}\text{C}$). Error bars on experimental data indicate one standard deviation as determined on three replicate specimens. Simulation results for three individual replicates based on the “complete” characterization of cement 152 are presented.

4. Conclusions

A prototype virtual test method for the heat of hydration of ordinary portland cement has been presented. By combining an early-age experimental measurement of chemical shrinkage with simulations conducted using the CEMHYD3D v3.0 computer model, a successful prediction of 7 d and 28 d heat of hydration can be achieved within 1 d of physical/virtual testing. Specifically, using the prototype virtual test method, the 7 d and 28 d heat of hydration of an ordinary portland cement

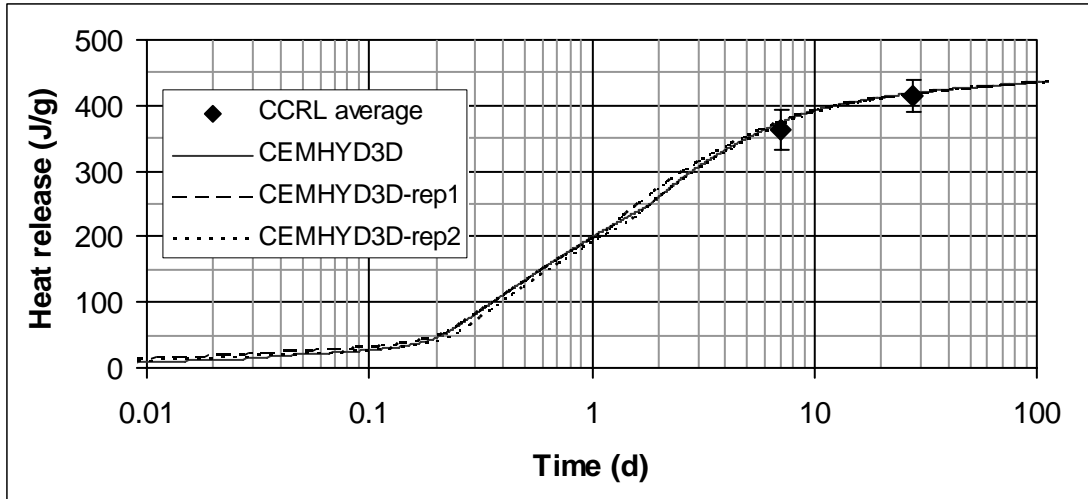


Figure 4. Measured and CEMHYD3D predicted heat of hydration for CCRL cement 152 ($w/c=0.4$, $23\text{ }^{\circ}\text{C}$). Error bars indicate one standard deviation as determined in the CCRL testing program.

can be generally predicted within one standard deviation of the mean value determined in a typical CCRL proficiency sample testing program. This level of accuracy for the virtual test method was obtained both when a “complete” PSD/SEM/X-ray characterization of the cements was performed and also when only their PSD and volumetric phase compositions were measured in a “simpler” characterization.

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