

3.2 “Time Domain Reflectometry Complex Permittivity Measurement in Hydrating Cement Systems for Determining Chemical State of Water”

N.E. Hager III and R.C. Domszy
Material Sensing & Instrumentation
772 Dorsea Rd. Lancaster PA 17601, USA

Abstract

Previous laboratory work demonstrated a continuous monitoring of the chemical state of water in hydrating cement paste over the frequency range 10 kHz to 8 GHz and from initial mixing to several weeks cure. The broadband complex permittivity was obtained over this range using Time-Domain-Reflectometry (TDR) Dielectric Spectroscopy, using Fourier transform methods and an embedded capacitance sensor. Three fundamental signals were identified, corresponding to unreacted free water appearing near 10 GHz, bound-water attached to developing microstructure near 100 MHz, and grain polarization occurring around 1 MHz. The three signal components were fit to appropriate molecular models as a function of cure time and monitored throughout the process. The results were 1) a free-water relaxation which monitored the disappearance of water into hydration and thus follows percent hydration, and 2) a bound-water relaxation which monitored water attaching to developing microstructure and thus monitors formation of this microstructure, and 3) a grain-polarization component which monitored developing microstructure.

The work presented here focuses on investigating changes in this relaxation spectrum and its cure evolution with changes in chemistry and processing conditions. Using the full frequency transform, we explore relative changes in various signal components with changes in ionic strength and backfilling of the pore space with excess free water. Monitoring the transient amplitude directly, we follow specific frequency components by monitoring corresponding delay times and follow reaction rates in the time domain. Changes in reaction rate are compared for changes in temperature, addition of accelerants and retarders, and other factors. Reaction rates obtained by TDR are also compared with rates obtained by other measures of cement hydration; such as with heat evolution obtained by isothermal calorimetry and calcium hydroxide production by differential scanning calorimetry. The transient analysis can be integrated with a small portable TDR sampler to form a robust cure-monitoring system usable in the field. Methods described should have broad applications in a variety of inorganic/organic materials and aqueous systems of interest in soil water characterization.

1. Introduction

The compressive strength of concrete and its loading capabilities are directly related to the ratio of water to cement solids (w/c) and degree of hydration in the cement paste, and to a lesser extent the size, shape, and strength of the aggregate used. The initial w/c ratio of the mix is the largest single factor influencing the strength of compacted concrete¹ and a continuous measure of w/c ratio during cement cure is known to be a predictor of concrete strength.^{2,3,4} Concrete with lower water/cement ratio (down to 0.35) makes a stronger concrete than a higher ratio, and certain chemical additives such as water reducers strengthen concrete by allowing a flowable concrete with less water than without such additives. The ability to accurately quantify the water to cement ratio and degree of hydration in the cement paste is an important benefit in characterizing strength and service life of concrete structures.

The research presented here explores a new method of monitoring hydration in cement and concrete materials⁵. The material is embedded with an inexpensive capacitance sensor and interrogated by broadband Time-Domain-Reflectometry (TDR) Dielectric Spectroscopy, providing a molecular rotation spectrum of water over an extremely wide frequency range. Three separate states of water participating in the hydration reaction are identified, including a free-water rotational state, a bound-water rotational state, and an ion-hopping state. The 3 states are fit to appropriate models as a function of cure time, and a variation in cement chemistry reveals the nature of the processes involved.

A unique aspect of the system is that the measurement is performed in the time domain, where sensor response is separated from instrument artifacts by propagation delay. Data can be either transformed to a microwave frequency spectrum for scientific-quality analysis, or interpreted directly in the time domain for robust field-grade control. This simplifies the measurement for field implementation, where the amplitude of the reflected transient can be followed directly without phase-sensitive frequency transform using inexpensive PC-based instruments.

2. Experimental Methods

The expressions governing TDR Dielectric Spectroscopy are described in the literature.⁶ The sample permittivity $\epsilon^*(\omega)$ is related to the Laplace Transforms of the incident $v_o(\omega)$ and reflected $r(\omega)$ pulses according to:

$$\epsilon^*(\omega) = \frac{G_c}{i\omega C_o} \frac{[v_o(\omega) - r(\omega)]}{[v_o(\omega) + r(\omega)]} \quad (1)$$

where C_o is the geometric capacitance of the empty sensor, G_c the characteristic line admittance, and ω the frequency. Refinements including bilinear calibration and nonuniform sampling are described in the literature.⁷

The sensor is a 3.6 mm diameter semi-rigid coaxial line with a short section of inner conductor protruding at its tip (Figure 1). Since the exposed tip is an effective radiator in high-permittivity liquids, it is shielded with a serrated castle nut, which provides a surrounding ground plane while allowing free-flow of material through the tip.

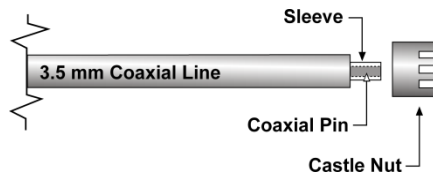


Figure 1 – Schematic of cement sensor.

A reference portland cement was obtained from the Cement and Concrete Reference Laboratory (CCRL) at NIST. The material is an ASTM Type I ordinary portland cement with a Blaine fineness of 394 m²/kg.^{8,9} Starting powders are mixed with distilled water in a water-to-cement ratio of 0.4 by weight.

The sample is placed in a sealed container with the sensor line extending through a rubber septum in the lid. Samples are placed in a temperature-controlled water bath with thermocouples recording the temperature. Data is acquired every 10-15 minutes initially, then slowed after several days cure. Acquisition is PC-automated, with all data records, calibration records, temperature, and timestamps stored in a common datafile for later analysis. A typical cure run records 300 individual records as a function of cure time, so monitoring is essentially continuous.

3. Frequency Domain Methods

Monitoring of Cement Hydration Figure 2 shows the real and imaginary permittivity during the cure of portland cement over the frequency range 10 kHz to 8 GHz. The initial real permittivity ϵ' on the left shows a broad flat region above 10⁷ Hz due to free-water response and a large increase below 10⁷ Hz due to electrode polarization. During the cure process, the high-frequency permittivity near 10 GHz decreases as free water is consumed in the reaction, while an intermediate-frequency signal grows around 1 MHz indicating reaction products forming during the process.

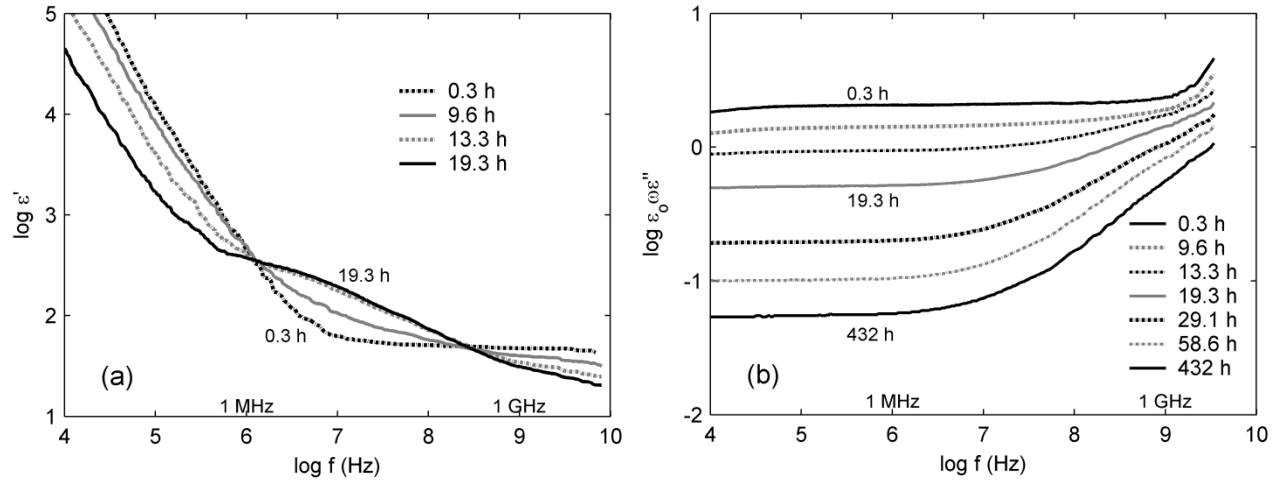


Figure 2 – Real and Imaginary Permittivity evolution during portland cement cure

The imaginary permittivity is displayed as dielectric conductivity $\epsilon_0\omega\epsilon''$ to remove the ω^{-1} dependence and accentuate small differences above 1 MHz. The initial conductivity on the right shows a large flat baseline across the frequency range representing DC conductivity. As cure proceeds the conductivity decreases, as seen by the decreasing baseline, and an intermediate-frequency signal grows as a deviation from the baseline around 100 MHz indicating reaction products forming during the process.

The intermediate-frequency signals are not present in the initial cement paste but only appear after several hours cure, indicating some additional states forming with developing microstructure. Signals appearing in permittivity and conductivity show separate relaxation frequencies, and are not real and imaginary counterparts of one another. We thus have two intermediate-frequency signals, each with permittivity and conductivity components, which we designate the low and medium relaxations.

Separation of Model Components A typical model fit is shown in Figure 3, where a broad Cole-Davidson relaxation and two narrow Debye relaxations are fit across the entire frequency range. Both real and imaginary components are fit simultaneously using shared parameters, with the frequencies, amplitudes, and distribution factors extracted as a function of cure time. For the real permittivity in (a), the model replicates the electrode polarization below 1 MHz, the low relaxation from 1 MHz to 1 GHz, and the free relaxation above 1 GHz. The fit is superimposed on the measured data along with individual model contributions. For the conductivity in (b), the model replicates the conducting baseline below 10 MHz along with the upturn above 10 MHz due to the medium and free relaxations. The fit is again superimposed on the measured data along with individual contributions, and it

is clear that the medium relaxation is required to replicate the conductivity behavior. Their evolution is now monitored

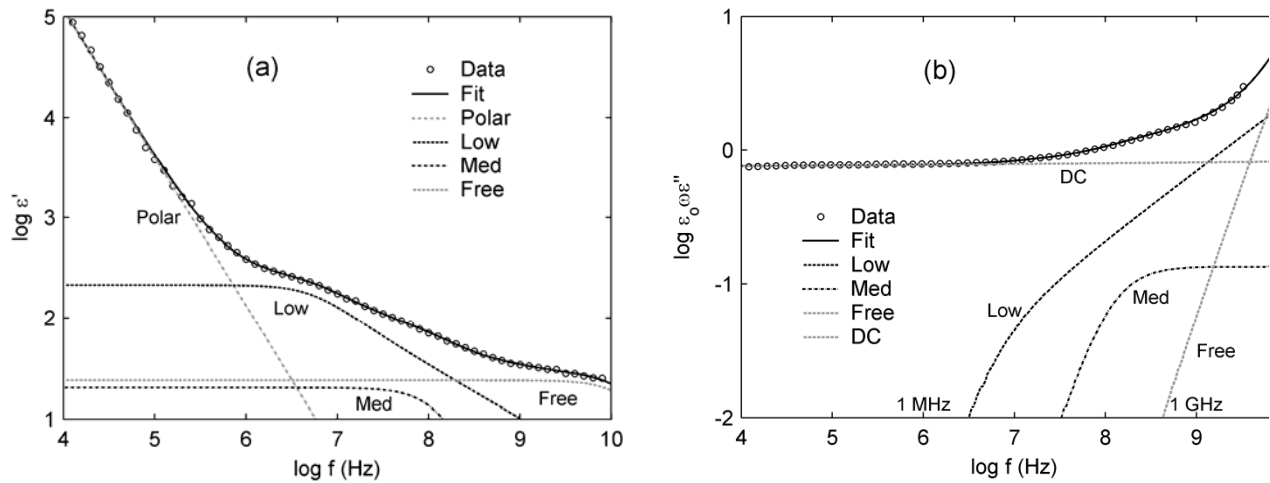


Figure 3 – Model fitting to real and imaginary permittivity at 15 h cure

continuously during the cure process by fitting the model continuously as a function of cure time.⁵

4. Frequency Domain Examples

Relative changes in the broadband frequency spectrum with chemical and physical changes are used to elucidate the nature of the processes involved. A variation in ionic strength of the fresh cement paste prior and a backfilling of the pore space with excess free water provide two such examples. A variation in temperature as various cure signals are established is another potential example.

Variation of Ionic Strength The low relaxation is significantly affected by a varying ion content⁵, either by substituting tricalcium silicate as the hydrating paste or by comparing tricalcium silicate with varying ion content. This is seen in Figure 4a where a tricalcium silicate sample is hydrated with and without potassium sulfate. The low-relaxation amplitude increases with increasing ion concentration, yet retains a relaxation distinct from DC conductivity. We attribute this to a grain-polarization model similar to McCarter,^{10,11} in which double layer processes operating on the gel surface increase the polarizability at frequencies just above electrode polarization. The medium relaxation is relatively unchanged, and we attribute this to bound-water model similar to van Beek,¹² in which water binds to developing microstructure and takes on a relaxation distinct from pure water. Similar behavior is seen in many organic/inorganic systems.^{13,14,15}

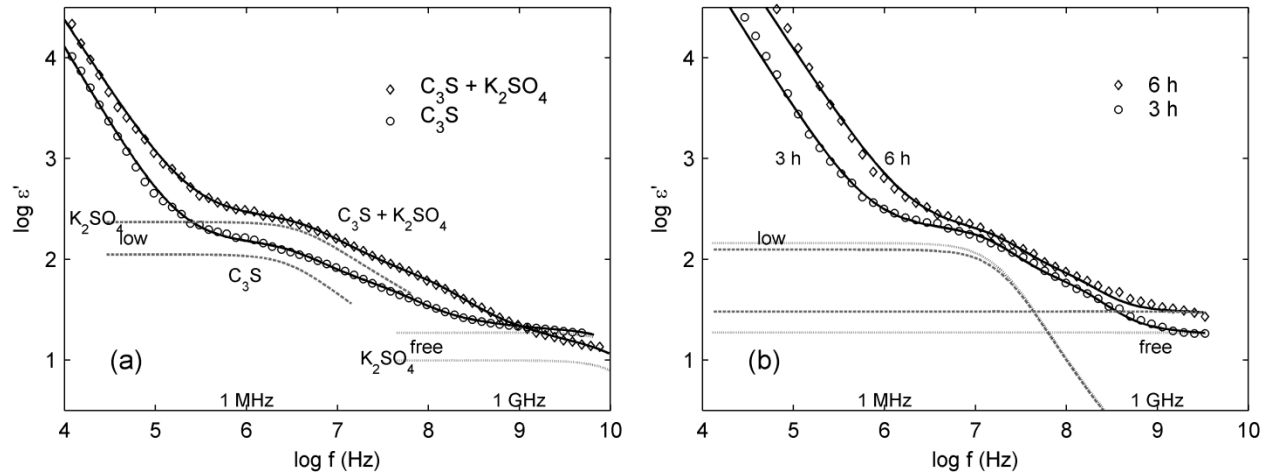


Figure 4 - Effect of ionic strength and excess pore water at ~24 h cure.

Variation of Pore Water The free-water and ion conductivity contributions are significantly affected by addition of excess pore water while the low relaxation remains relatively constant. This is seen in Figure 4b where a 50 mm mortar cube with a sensor at its center is submerged in water at 24 h cure. Both the free-water permittivity near 10 GHz and the electrode polarization below 100 kHz increase over a period of 6 hours, as the sample remains submerged and water fills the pore space. The increased electrode polarization reflects an increased conductivity in the sample, while the low relaxation remains relatively unchanged. Pore water variation thus reflects the inverse of ionic strength variation, as the low relaxation remains relatively constant.

5. Time Domain Methods

TDR offers an advantage over frequency-domain methods in that the rate-dependent information can be interpreted directly in the time domain. From Fourier analysis, the 10 GHz response is concentrated near the peak of the reflected transient in the picosecond range, while ~100 MHz and ~1 MHz response is concentrated at later times in the transient in the nanosecond/ microsecond ranges. By monitoring the amplitude near the transient peak we monitor the 10 GHz permittivity indirectly, and thus follow the free-water concentration exclusively, since other effects including bound water and ion conduction cannot respond at these frequencies.

Separation of Permittivity and Conductivity in Test Fluids An example is shown in Figure 5. A sensor is inserted in a test fluid and interrogated with a 35 ps pulse with the response displayed on a logarithmic time scale. On the left the test fluid is varied among dielectric reference liquids of increasing permittivity, from dichloromethane ($\epsilon' = 8.9$), to acetone ($\epsilon' = 21.1$), to acetonitrile ($\epsilon' = 37.5$), to deionized water ($\epsilon' = 78$). The

reflected signal shows an increasing amplitude with each liquid on the 100 ps time scale, since each liquid has a fast dipole rotation which can respond at these speeds. On the right the deionized water is measured again, but now with increasing amounts of salt concentration. The initial increase at short times remains unchanged, but now an additional loading is seen on longer time scales due to slow-responding conducting ions. The short-time permittivity is dependent on material and independent of conductivity, so the response is chemical-specific.

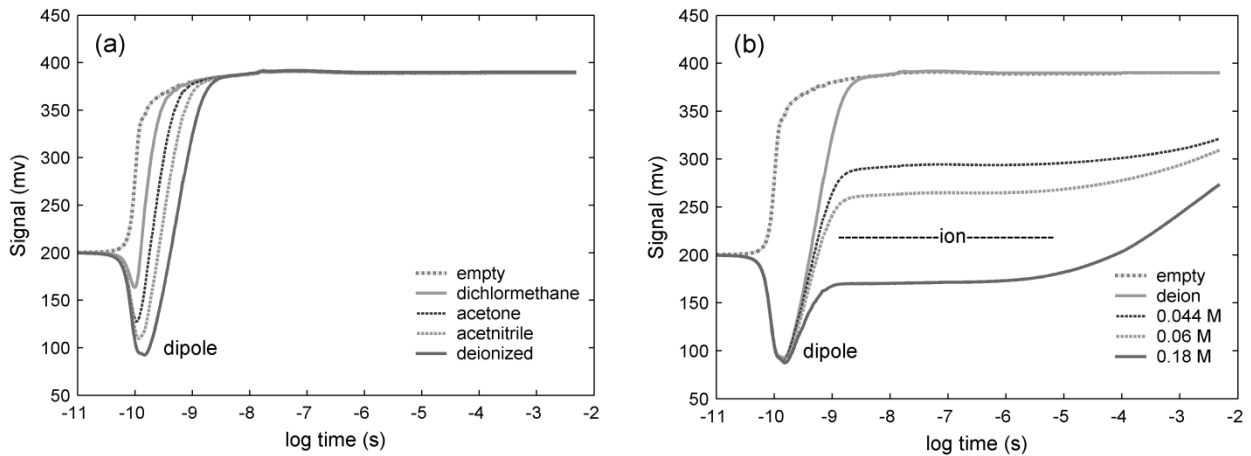


Figure 5 – TDR reflection for (a) varying permittivity (b) varying conductivity

Separation of Components in Portland Cement Figure 6 shows the direct transient for portland cement from which Figure 2 is derived. The signal is captured on 7 successive time scales, beginning at 20 ps/cm on the left and ending at 500 μ s/cm on the right. The transient is displayed on a piecewise-linear scale where multiple relaxations at intermediate times are more easily seen. The transient is inverted in the usual manner, showing the empty-sensor reflection at the top and two constant-permittivity reference liquids ($\epsilon' = 21.1, 37.5$) below. The reference liquids show an exponential decay indicating a constant sensor capacitance in series with the 50-ohm line. Also shown is the cement paste, which shows a superexponential decay spanning many decades due to the varying sensor capacitance. At 1 hour the transient shows a large amplitude on the 20 ps/cm timescale, indicating free-water activity, followed by a long baseline on later timescales indicating ion conduction. At 20 hours the transient shows a smaller amplitude on 20 ps/cm timescale, indicating reduced free-water activity, followed by a continuing decay on later timescales indicating additional relaxations. The conducting baseline decreases with decreasing ion conductivity.

A simple indicator for the free relaxation is the amplitude on the 20 ps/cm scale near the peak of the reflected signal. The delay time is approximately 100 ps, representing response in the gigahertz frequency range ($\omega = 1/t$). A

simple indicator for the low relaxation is the amplitude on the 500 ps scale, where the reference transients have decayed to zero yet continuing cement decay is seen. The delay here is around 1 ns, representing response in the sub-gigahertz frequency range. To remove conductivity the baseline at 100 ns is subtracted, leaving a difference signal above the conductivity which cannot be accounted for by free-water relaxation.

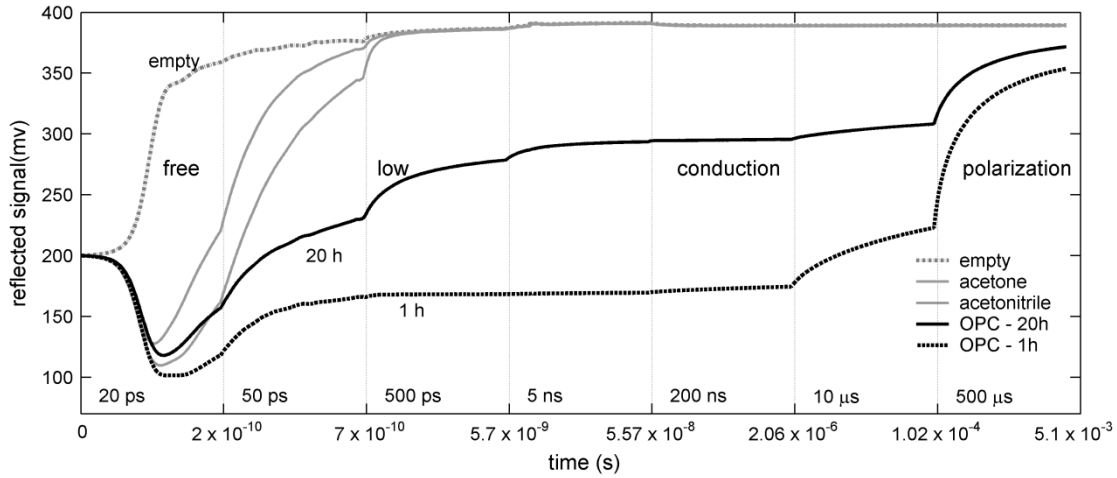


Figure 6 - TDR reflected transient over 7 times scales during cement hydration

6. Time Domain Examples

Pore-Water Monitoring The backfilling of pore water into a fully cured 50 mm mortar cube was monitored with a sensor embedded in its center. Figure 7 shows 100 ps amplitude as a function of time after the dry cube is submerged in a water bath. The signal is stable for around 30 hours, and then begins to increase on the inverted axis as water fills the pore space. At longer times the rate of change slows and begins to level off. A similar plot at 1 μ s delay - where ion conduction dominates - shows a completely different signal evolution.

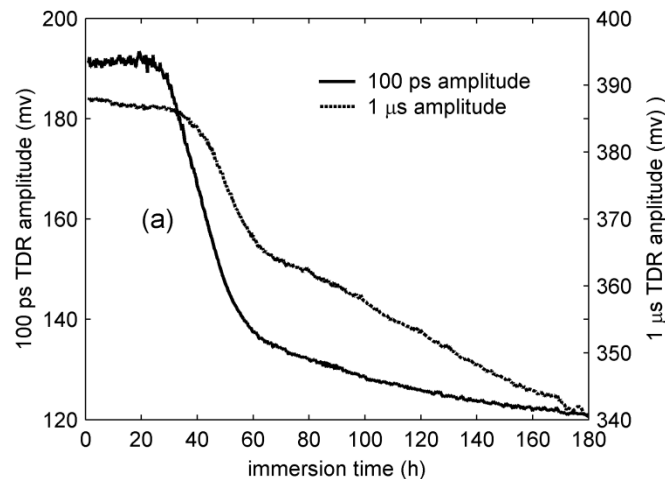


Figure 7 – 100 ps transient amplitude during backfilling of 50 mm mortar cube

Cement Cure Monitoring Since the free-relaxation indicator scales with free-water concentration, and the low-relaxation indicator scales with microstructure formation, these simple indicators can be used to study variations in reaction rate between different cement formulations and cure conditions. This can be used to analyze the effects of temperature, water-to-cement ratio, particle-size distribution, addition of retardants and other changes on cure evolution. In addition, these indicators can be used with a simplified TDR electronics package to form a robust cure-monitoring system usable in the field. We consider some examples of changes which can be monitored:

Variation in Temperature The free- and low-relaxation indicators show the variation in hydration rate with changing cure temperature. Figure 8a shows the evolution of both indicators for two portland cement pastes undergoing cure at different temperatures. One sample is at $23.0 \pm 0.5^\circ\text{C}$ and the other at $30.0 \pm 0.5^\circ\text{C}$. The 30°C sample shows a faster decay of the free-relaxation indicator, as well as a faster growth of the low-relaxation indicator and an earlier signal maximum. All other changes are roughly the same in both cases.

Addition of Retarders The free- and low-relaxation indicators also show a decrease in hydration rate with the addition of chemical retarders. Figure 8b shows the evolution of both indicators for two portland cement pastes undergoing cure under identical conditions, with one sample prepared neat and the other containing 288 ppm sodium gluconate retarder. The retarder sample shows a slower decay of the free-relaxation indicator, as well as a slower growth of the low-relaxation indicator and a later signal maximum. Both samples are prepared using CCRL 135 portland cement in a w/c ratio of 0.42, with both containing F-35 sand in a ratio of 1:1 and cured at 22°C.

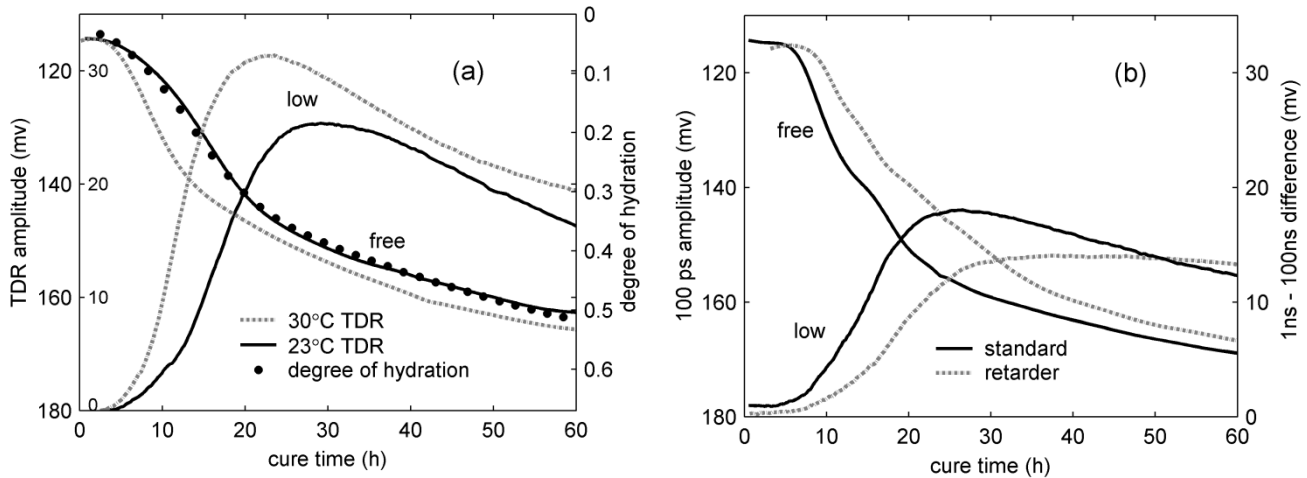


Figure 8 – Temperature Variation and Addition of Retarders

Comparison with Heat of Reaction The free-relaxation amplitude can be correlated with the exothermic heat of reaction as measured by isothermal calorimetry. The results are shown in Figure 8a, where the heat of hydration determined from calorimetry is normalized by the published volumetric phase compositions of portland cement⁸ and the known values of the heat of hydration of the major phases in cement.¹⁶ It is clear that the 100 ps transient amplitude follows a similar evolution with cure time, with the amplitude scaling and offset adjusted for convenience.

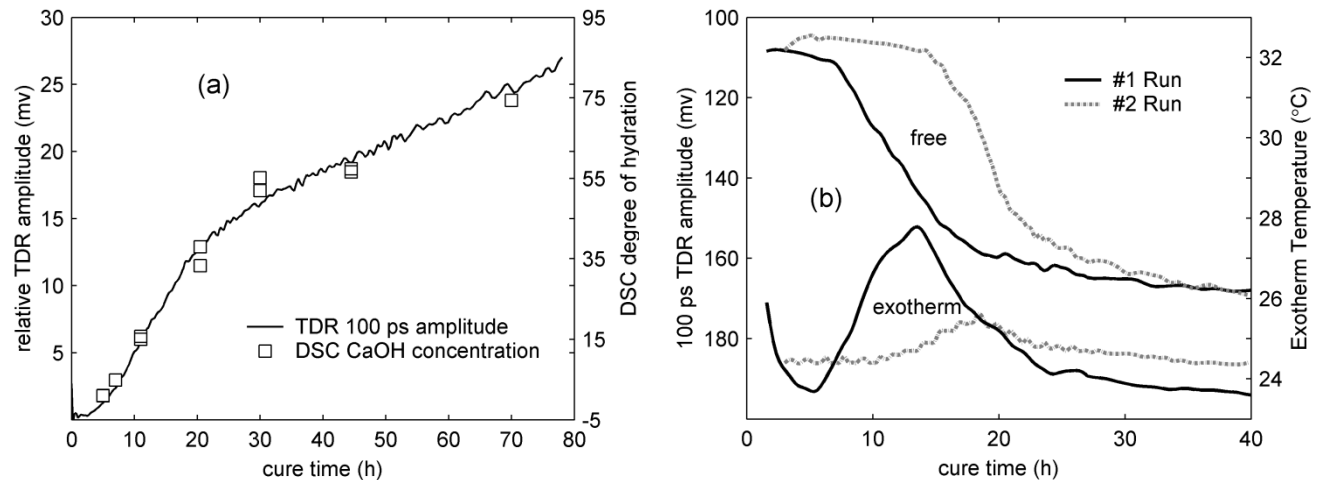


Figure 9 – DSC comparison and Field Concrete Exotherm

DSC Comparison with CaOH Production The concentration of free water being consumed in reaction can be compared with the concentration of calcium hydroxide produced by reaction as measured by Differential Scanning Calorimetry (DSC). For each TDR sample 12 side-samples are extracted to sealed centrifuge tubes, and stored in the bath along with the TDR sample. Samples are opened at regular intervals and a Perkin-Elmer DSC System 4 used to determine the calcium hydroxide content. Hydration is blocked in individual samples at specified times by grinding in the presence of acetone, filtering on a glass filter, rinsing the residue, and transferring to a vacuum oven. Figure 9a shows the TDR 100 ps amplitude plotted in solid lines and the DSC endotherm plotted in symbols, with the vertical scaling and offset between axes adjusted for best fit.

Exotherm Comparison in Precast Concrete The free-relaxation has been monitored in production grade concrete from a nearby precast plant. A bucket is obtained from the plant and returned immediately to the lab with a sensor and thermocouple probe inserted. The Fourier-transform spectrum is verified, showing the same free, bound, and polarization components as in cement paste, albeit with reduced amplitude due to the lower water/solids ratio. Figure 9b shows the TDR amplitude for 2 different batch runs compared against the reaction exotherm, and it is clear the maximum reaction exotherm corresponds to maximum rate of free water disappearance by TDR.

7. Conclusions

Time-Domain-Reflectometry Dielectric Spectroscopy provides a continuous monitor of the chemical state of water in hydrating cement materials over the frequency range 10 kHz to 10 GHz and from initial mixing to long-time cure. Three fundamental signals are identified, corresponding to unreacted free water appearing near 10 GHz,

bound-water attaching to developing microstructure near 100 MHz, and grain polarization occurring around 1 MHz. The three signal components are fit to appropriate molecular models as a function of cure time and monitored throughout the process.

We can use this behavior to explore variations in cement chemistry and processing conditions. Using the full frequency transform, we show an increase in grain polarization with increases in ionic strength, and an increase in free water and electrode polarization with backfilling of the pore space with excess free water. Monitoring the transient amplitude directly, we follow variations in reaction rate with changes in temperature and addition of chemical retarders. We compare reaction rates with other measures of hydration, such as heat evolution by isothermal calorimetry and calcium hydroxide production by differential scanning calorimetry. We monitor backfilling of the pore space with excess water over long periods of time and monitor the cure of precast concrete obtained from production runs.

Future work will explore a variety of signal changes occurring in each component with material and processing changes through a combination of analytical measurement, chemical variation, and experimental investigation.

Acknowledgements

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