

Early Hydration of Portland Limestone Cements Monitored by Raman Spectroscopy

Dylan J. Freas
Chemistry, Williams College

NNIN REU Site: Institute for Electronics & Nanotechnology, Georgia Institute of Technology, Atlanta, GA
NNIN REU Principal Investigator: Dr. Kimberly E. Kurtis, Civil and Environmental Engineering, Georgia Institute of Technology
NNIN REU Mentor: Elizabeth I. Nadelman, Civil and Environmental Engineering, Georgia Institute of Technology
Contact: dylan.j.freas@williams.edu, kimberly.kurtis@ce.gatech.edu, enadelman3@gatech.edu

Abstract:

Given its innate heterogeneity, cement hydration is a difficult process to study, and many current techniques have limited use in identifying specific chemical changes that occur during the hydration process. Raman spectroscopy has the potential to supply this information. This study was aimed at evaluating the capability of Raman spectroscopy in studying the hydration of Portland limestone cements. The consumption of many raw cement phases and the formation of major cement hydration products were detected over various time periods of hydration. This information provides insight on the nanostructural development of concrete, which can be correlated to the evolution of its macroscopic properties.

Introduction:

Globally, the cement industry accounts for approximately five percent of current anthropogenic carbon dioxide (CO₂) emissions [1]. The source of most of the CO₂ emissions during cement manufacturing is the heating of raw materials, such as limestone and clay, to form cement clinker. One method the cement industry has implemented to reduce CO₂ emissions is replacing a portion of cement clinker with filler material such as limestone. However, it is crucial to understand the effect of limestone addition on the hydration and microstructural development of cement.

Raman spectroscopy is a relatively innovative technique in the field of pure cement study. One of the most significant features of this technique is its capability for a real-time *in situ* analysis. Using this technique, researchers have characterized individual clinker components, studied the progress of timed hydration on various clinker phases, and identified products of Portland cement hydration [2]. The purpose of this present study is to extend Raman spectroscopy to the characterization of Portland limestone cements and to demonstrate its ability to characterize the formation of hydration products at the nanoscale.

Experimental Procedure:

Type I/II ordinary Portland cements containing ~3% limestone (“AI”) were compared to Type IL Portland limestone cements containing ~12% limestone (“AL”). The cements were mixed with deionized water at a water-to-cement ratio of 0:4. The

cement pastes were stored in microscope well slides, and cover slips were sealed over the pastes in order to reduce the effect of carbonation.

Raman spectra were collected using a Thermo Almega XR Micro and Macro Raman Analysis Spectrometer with a 488 nm laser. A circular spot size of 50 μm was used at 50x magnification. The Raman shift range chosen for study was 200-1200 cm⁻¹ with 40 seconds exposure. All instrumental configuration was systematically chosen by targeting for a high S/N ratio and statistical representativeness.

The collected data were processed using Thermo Scientific’s OMNIC Series software. The qualitative analysis of cement hydration was performed on the data normalized to the signal with the largest Raman intensity value. Baseline correction and cover slip subtraction were also applied in the data analysis.

Results And Discussion:

The Raman spectra for the two cement pastes are shown in Figures 1 and 2. Peaks were identified using values reported in the literature [3]. The results show that many major phases of commercial cement, such as limestone, gypsum, and tricalcium silicate and dicalcium silicate (C₃S / C₂S), can be detected, along with many major cement hydration products, including ettringite, calcium hydroxide (CH), and calcium silicate hydrate (C-S-H).

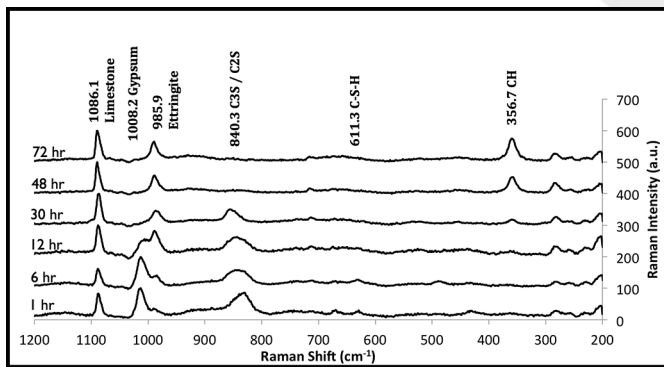


Figure 1: Time-lapsed Raman spectra of a Type IL Portland limestone cement (AL).

For both cement pastes, the C_3S/C_2S bands from ~ 800 - 900 cm^{-1} become shifted toward 860 cm^{-1} by 30 hr, which corresponds to the initial rapid hydration of C_3S , leaving primarily C_2S . By 48 hr, the C_2S signal has disappeared, indicating the consumption of both calcium silicate phases. The formation of CH ($\sim 356\text{ cm}^{-1}$) is detected by 24 hr and its principal band increases in intensity through 72 hr. C-S-H was not clearly detected, but the broad C-S-H band between 600 - 700 cm^{-1} is seen to increase in intensity over time as more C-S-H is produced.

The conversion from gypsum ($\sim 1008\text{ cm}^{-1}$) to ettringite ($\sim 988\text{ cm}^{-1}$) is illustrated as early as 6 hr and continues through 24 hr, at which point the gypsum signal has disappeared and the ettringite band continues to increase in intensity. This trend continues through 72 hr. The gypsum band is not as pronounced in the Type I/II ordinary Portland cement paste as it is for the Type IL Portland limestone cement paste because the corresponding raw cement contained less gypsum prior to hydration.

Conclusions and Future Work:

This research shows that Raman spectroscopy can effectively characterize the hydration of Portland limestone cements. This nondestructive technique has been shown to provide results that are consistent with those from previous studies of cement hydration, including calorimetry and Fourier transform infrared spectroscopy studies [4]. Future work will correlate Raman spectroscopic signatures with morphological information obtained by scanning electron microscopy and specific surface area analysis, chemical composition information obtained by thermogravimetric analysis, and reaction kinetics information

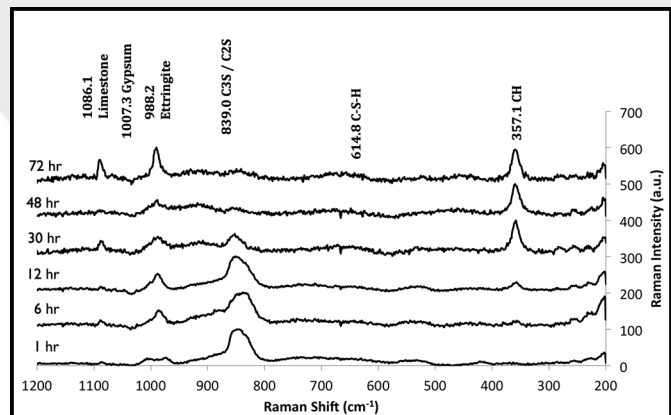


Figure 2: Time-lapsed Raman spectra of a Type I/II ordinary Portland cement (AI).

provided by isothermal calorimetry, to obtain a comprehensive understanding of the nanostructural development of cement-based materials.

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References:

- [1] Lollini, et al. Effects of Portland Cement Replacement with Limestone on the Properties of Hardened Concrete. *Cement & Concrete Composites*, 2014, 46, 32-40.
- [2] Garg, et al. A Raman Spectroscopic Study of the Evolution of Sulfates and Hydroxides in Cement-Fly Ash Pastes. *Cement and Concrete Research*, 2013, 53, 91-103.
- [3] Potgieter-Vermaak, et al. The Application of Raman Spectrometry to Investigate and Characterize Cement, Part I: A Review. *Cement of Concrete Research*, 2006, 36, 656-662.
- [4] Ylmen, et al. Early Hydration and Setting of Portland Cement Monitored by IR, SEM, and Vicat Techniques. *Cement and Concrete Research*, 2009, 39, 433-439.