Quantitative Determination of Calcium Hydroxide by Using Near-Infrared Spectroscopy

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Abstract. Calcium hydroxide (CH) is a by-product from hydration reaction of cement along with calcium silicate hydrate (C-S-H) gel. It helps to protect the steel reinforcements in concrete structures from corrosion process due to carbonation. The presence of calcium hydroxide provides a basic environment (pH>10) that induces the formation of passive oxide film and keeps steel structures from corrosion. The detection and quantification of calcium hydroxide in concrete structures are important to understand the nature and state of the steel structures in concretes. In this research work, the variation of calcium hydroxide to calcium silicate ratios in cement were measured by using near-infrared spectroscopy (NIR). The first overtone of the OH groups in calcium hydroxide absorbs at 7082 cm^{-1} and this absorption peak can be used as a quantitative measure of calcium hydroxide in samples. Correlation plot between second derivative absorbance intensity at 7082 cm^{-1} with different mixtures of calcium hydroxide in calcium silicate base. The amount of calcium hydroxide in calcium silicate base was established. This calibration plot was used as basis for determining calcium hydroxide content in unknown concrete samples. Concrete samples for the quantitative determination of calcium hydroxide were prepared from standard cement samples and cement samples with or without pozzolan along with various water to cement ratios. The results show that all samples analyzed in this work contain calcium hydroxide in varying amounts. This variation reflects the composition of the cement and concrete samples.

Introduction

Concrete is one of the most widely used construction material in the world that made up of cement and aggregates, such as sand, gravel, and crushed stone, along with water to bind them together [1]. Cement is composed of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), gypsum (CSH_2). Cement is hardened when mixing with water called hydration reaction, and cement properties depend on water to cement ratio (w/c) [2-3]. Calcium silicate hydrate (C-S-H) gel is produced around the cement particles which provide the cement strength along with calcium hydroxide (CH or portlandite). Hydration reaction model have been studied by *Mindress et al.,* 2002 [4-5]. Likewise, calcium hydroxide is also generated in the reaction and its advantage is to promote the formation of passive oxide film that cover the steel reinforcements and prevent them from the corrosion process. This passive oxide film will no longer stable when carbon dioxide penetrates through the empty pore of concrete and reacts with calcium hydroxide to form calcium carbonate ($CaCO_3$) called carbonation reaction [6-11]. Corrosion occurs by an electrochemical process following by rust formation. Then, internal stress of the concrete will increase to cause concrete cracking and spalling. To prevent the corrosion of reinforcement in time, exactly amount of calcium hydroxide needs to be measured. Quantitative determination of calcium hydroxide has been investigated by *Saeki et al.* and *Biernacki et al.* Unfortunately, $CaCO_3$ will also be detected, and low accuracy when using thermogravimetric analysis (TGA) and quantitative X-ray diffraction (QXRD), respectively [12-13]. Recently, near-infrared spectroscopy (NIR) was used to investigate hydration reaction of cement. An interesting peak at 7082 cm^{-1} was observed, which belongs to the first overtone of the OH stretching of the OH groups present in calcium hydroxide [14-16]. Therefore, quantitative NIR spectroscopy becomes an interesting method to determine the amount of calcium hydroxide in cement and concrete samples. Second derivative profile was calculated to remove the background, the spectrum was sharper, and clearer to interpret.

Experimental

Chemicals (calcium hydroxide and calcium silicate) were purchased from commercial suppliers (Aldrich Chemistry), they were used without further purification. Standard cement was purchased from commercial suppliers (Ultipro). NIR spectra were recorded on Perkin Elmer spectrum One NTS, FT-NIR system (10000-4000 cm^{-1}) equipped with a transflectance accessory and a DTGS detector. A total of 20 scans were made at a resolution of 16 cm^{-1} on each sample.

Sample preparation. Various calcium hydroxide to calcium silicate ratio were prepared and measured by using NIR spectroscopy. Second derivative profile was calculated, and second derivative absorbance intensity was plotted with concentration of CH. Three cement samples with various w/c ratio (0.35, 0.40, 0.45, 0.55) were prepared. They were hardened for 7, 14, and 28 days and measured by using NIR spectroscopy. Concrete samples were also prepared by mixing with sand and different w/c ratio (0.36, 0.41, 0.48, 0.52). They were hardened under water for 2 days at 60°C and measured by using NIR spectroscopy.

Results and Discussion

Different calcium hydroxide to calcium silicate ratios were characterized by using FT-NIR spectroscopy. Two prominent peaks were observed, which are the peak at wavenumber 5200 and 7082 cm^{-1} indicate water molecule that is absorbed on the surface and first overtone of OH stretching of calcium hydroxide, respectively. Absorbance spectrums were converted to second derivative profiles. Fig. 1 shows that the highest amount of calcium hydroxide, the highest intensity is observed. Second derivative absorbances of calcium hydroxide were measured in the absolute value.

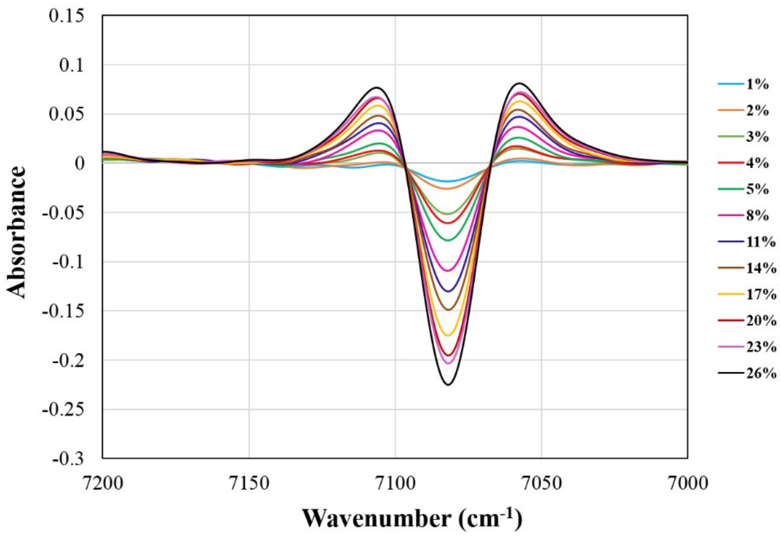

Fig 1. Second derivative FT-NIR spectrum of calcium hydroxide at 7082 cm^{-1}

Calibration graph between concentration of calcium hydroxide and second derivative absorbance intensity at wavenumber 7082 cm^{-1} were plotted into two graphs due to trend changing. Fig. 2 is the calibration curve of 0.01 to 0.08 calcium hydroxide to calcium silicate ratio, which linear equation is y = 1.3156x along with linearity (R^2) is 0.9873. On the other hand, linear equation y = 0.6543x + 0.0656 with linearity (R^2) is 0.9925 for the calibration curve of 0.10 to 0.26 calcium hydroxide to calcium silicate ratio as shown in Fig. 3.

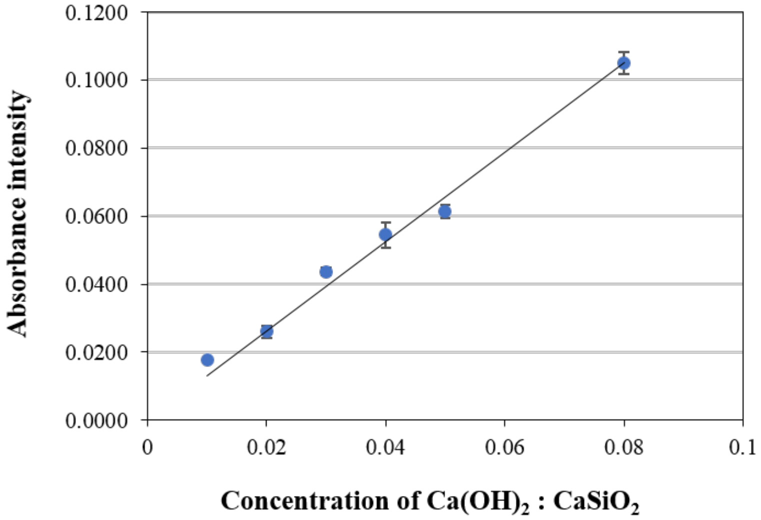

Fig 2. Calibration curve of 0.01 to 0.08 calcium hydroxide and calcium silicate ratio, linear equation y = 1.3156x, R^2 = 0.9873

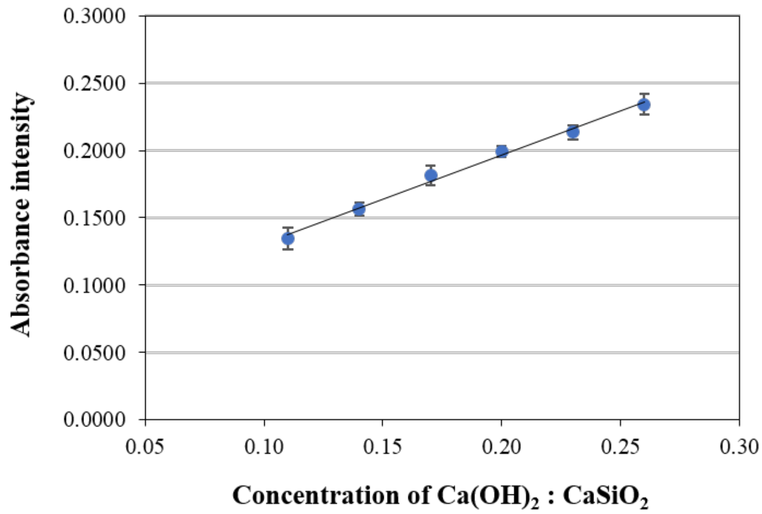

Fig 3. Calibration curve of 0.10 to 0.26 calcium hydroxide and calcium silicate ratio, linear equation y = 0.6543x + 0.0656, R^2 = 0.9925

Quantitative determination of calcium hydroxide in cement with and without pozzolan were investigated by varying w/c ratios, the results are shown in Table1. Each cement was characterized by near infrared spectroscopy. Second derivative profile showed a very sharp peak at 7082 cm^{-1} which belongs to O-H stretching of calcium hydroxide (CH). The absorbance was noted, and converted to percentage of calcium hydroxide in the cement samples. As you can see in entry 4, the highest amount of calcium hydroxide was obtained up to 6.8% when no pozzolanic cement mixed with 0.55 w/c ratio after only 7 days. Moreover, the amount of calcium hydroxide was decreased with time due to the formation of calcium silicate hydrate gel and there was no further hydration. The amount of calcium hydroxide in no pozzolanic cement was higher than the pozzolanic cement due to higher cement amount, which means there was more hydration reaction occured. Hydration reaction time of cement with and without pozzolan samples were the same as 7 days.

Table 1. The amount of $Ca(OH)_2$ in pozzolanic cement and no pozzolanic cement samples with various w/c ratios after curing for 7, 14, and 28 d.

entry	ratio	curing time	amount of CH [%]	
			pozzolanic cement	no pozzolanic cement
1	0.35	7 d	2.8352	3.8690
2	0.40		2.8124	4.7963
3	0.45		3.6029	5.2220
4	0.55		4.5911	6.7574
5	0.35	14 d	2.7060	4.6215
6	0.40		2.8808	4.4618
7	0.45		2.8276	5.6172
8	0.55		4.3706	6.6434
9	0.35	28 d	2.5008	4.2946
10	0.40		3.4661	4.1502
11	0.45		3.8690	6.0201
12	0.55		4.0286	5.9137

Furthermore, the variation of w/c ratios in concrete samples were studied by using 0.36, 0.41, 0.48, and 0.52 as shown in Table 2. All concrete samples were cured under water for two days called wet concrete. Then, concrete samples were dried under atmosphere for a week called dried concrete. Both wet and dried concrete were measured the amount of calcium hydroxide by using NIR spectroscopy. The results show that calcium hydroxide was produced in dried concrete up to 9.4% (entry 8) that is higher than the amount of calcium hydroxide in wet concrete which is only 6.8% (entry 4) along with w/c ratio equal to 0.52.

Table 2. The amount of $Ca(OH)_2$ in concrete with various w/c ratio

entry	ratio	absorbance intensity	amount of CH [%]
1	0.36	0.0998	7.5859
2	0.41	0.0833	6.3317
3	0.48	0.1008	7.6619
4	0.52	0.0892	6.7802
5	0.36	0.0902	6.8562
6	0.41	0.0998	7.5859
7	0.48	0.1133	8.6120
8	0.52	0.1233	9.3721

Conclusions

Quantitative near-infrared spectroscopy can be used to determine the amount of calcium hydroxide in cement and concrete samples. The first overtone of OH stretching of OH groups in calcium hydroxide was observed at wavelength 7082 cm^{-1}. Cement samples without pozzolans produced the highest amount of calcium hydroxide up to 6.8% after 7 days along with 0.55 w/c ratio. On the other hand, the amount of calcium hydroxide that was produced by hydration of pozzolanic cement with 0.55 w/c ratio was only 4.6% due to lower cement content. Concrete samples with 0.52 w/c ratio produced calcium hydroxide up to 9.4% after drying. Thus, the highest w/c ratio would generate the greatest amount of calcium hydroxide. Even through, the percentage of calcium hydroxide in cement and concrete samples was increased with time, part of it was used in the formation of calcium silicate hydrate gel.

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