Do Regular- and Nano-sized Hydrated Lime Have Different Mechanisms in Asphalt?

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Abstract: Currently, most highway agencies use hydrated lime, or specially referred as Regular-sized Hydrated Lime (RHL) as a multifunctional additive, especially to mitigate moisture damage of the asphalt mix. Previous physical studies by the authors have addressed the potential benefits of using the Nano-sized Hydrated Lime (NHL) over the RHL in the asphalt-aggregate system. However, the hydrated lime (RHL and NHL) mechanisms in asphalt-aggregate system, to be fully addressed, should be studied using physical and chemical investigations. One of the objectives this paper is to present a state-of-the-art of the mechanisms of hydrated lime in asphalt-aggregate system to highlight the aspects of such complex mechanisms based on previous studies performed on the RHL. Also, a developed methodology using the Fourier Transform Infrared Spectroscopy (FTIR) technique that was further supported by quantum chemical calculations was employed to quantify the hydrated lime reactive group (hydroxyl group, O-H) within the hydrated lime (RHL and NHL)-modified asphalt binder in an attempt to present a fundamental basis behind the effect of particle size on the chemistry of hydrated lime-asphalt system. In line with the physical results obtained from related studies, the hydrated lime particle size is a contributing factor to its functionality in the asphalt-aggregate system.

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Introduction

The transportation agencies look for appropriate modifiers for better performing asphalt materials. In recent years, the revolution in production of nanomaterials helped researchers find ways to pattern and characterize materials at the nanometer scale. The nanoparticles (nanomaterials) offer different physicochemical properties than the macroscopic particles and thus, can offer different functionalities for engineering purposes. The application of nanotechnology in pavement industry intends to advance the structure of the asphalt (both durability and stiffness) by the development of novel materials and the use of characterization methods to improve the understanding of these materials. Several preliminary studies have investigated the application of various nanomaterials which have been or have potential to be used in asphalt modification. Although, the RHL has been used extensively in hot mix asphalt for many years as a quality additive and/or filler, the usage of NHL (having at least one dimension \leq 100-nm) has not yet been initiated in

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pavement industries. A pioneer work by the authors [1-4] has been devoted to study the potential benefits of using the NHL over the RHL based on different physical testing results. Realistically, the mechanisms of hydrated lime in asphalt is a much more complex subject, especially with the application of nano-sized particles, that is worthy of more studies. The current study was initiated as a continuation of the previous studies [1-4] to demonstrate a chemical interpretation of the physical results, based on a developed methodology of the FTIR technique, and with support of the quantum chemical calculations. This paper first presents a background to draw attention to hydrated lime mechanisms in asphalt based on previous studies conducted on the RHL.

Background

The addition of hydrated lime to asphalt mixtures commonly is associated with a complex array of mechanisms with the asphalt-aggregate system. So far, the proposed mechanisms explaining the effects of hydrated lime on asphalt-aggregate systems remain somewhat hypothetical. The literature is rich of results and explanations showing several mechanisms of hydrated lime, some explain from adhesion point of view, others in terms of aging and yet some others in terms of mechanical properties. However, the hydrated lime has different complex levels of mechanisms in the mix that require a solid explanation and connectivity with the physical results. The addition of hydrated lime can modify the aggregate surface. Also, hydrated lime is reacting with some of the acidic moieties naturally present in the asphalt binder, which is referred to as the chemical effect between this basic compound and the weakly acidic nature of the asphalt binder. Additionally, the porous structure of hydrated lime results in some physical interactions. The following sections explain the mechanisms

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between the hydrated lime and asphalt-aggregate system based on previous studies conducted on the RHL.

Effect on Aggregate

The aggregate chemistry is a major contributing factor to the moisture susceptibility of an asphalt mixture [5]. It is well known that siliceous aggregates are more susceptible to stripping (i.e., hydrophilic) than limestone aggregates (hydrophobic) [6, 7]. Curtis et al. [5] explained the reasons the siliceous aggregates are more susceptible to stripping. Asphalt binder would be expected to adhere better to alkaline (basic) aggregates (opposite charges attract) such as limestone than to acidic siliceous aggregates. The presence of more silica contents in aggregates is results in their acidic nature, while more carbonate contents cause the basic nature. The calcium carbonate in the limestone reacts with the carboxylic acid in asphalt binder and forms a strong bond. On the contrary, siliceous aggregates are acidic in nature, therefore, no chemical bond is formed between the asphalt binder and aggregate. Water, being polar in nature, can easily displace the asphalt binder from the aggregate surface in the absence of a strong bonding, since the polarity of water is higher than asphalt binder. The addition of hydrated lime allows for the precipitation of calcium ions onto the aggregate surface, making it more favorable to asphalt binder and improves the binder-to-aggregate adhesion [8, 9]. This mechanism has been proposed by Ishai and Craus [8]. By the addition of hydrated lime to the mastic, calcium ions can precipitate on the aggregate surface and then bond with the acids from the asphalt binder, forming water-insoluble salts. However, the effectiveness of hydrated lime to improve the adhesion is not limited to the siliceous aggregates (as acidic aggregates), it improves the adhesion with basic aggregates (e.g., limestone) as well [10].

In case of the presence of clay fines on aggregate surface, the hydrated lime offers an additional mechanism. Clays are generally present in the form of small inclusions inside the rocks liberated upon crushing frequently coats the surface and is not completely removed during aggregate preparation prior to the mixing process. Contaminating the aggregates surface by large amounts of clays decreases the chances of adhesion between asphalt binder and aggregate, which in-turn increases the moisture susceptibility of the system due to the action of water. By the addition of hydrated lime it acts similarly as observed in soil treatment [11]. Hydrated lime flocculates the clay particles, preventing them to build a water-displaceable barrier between the asphalt binder and aggregate [12].

Effect on Asphalt Binder

Hydrated lime, $Ca(OH)_2$, is a strong base that reacts readily with acidic components such as carboxylic acid to form calcium salts that are virtually insoluble in the asphalt binder. Plancher and Peterson [13] found that 4–6% of the asphalt binder consisting of asphalt components containing the carboxylic acid and 2-quinolone types chemical function groups. The addition of hydrated lime helps the irreversible absorbance of these components onto the surface of the hydrated lime particles. These components were also found to be primarily a component of the asphaltene fraction of the asphalt

binder [14-17]. Removal of these components from the asphalt binder matrix by the adsorption on the hydrated lime particles helps increase the component compatibility of the asphalt binder consequently reducing its sensitivity to viscosity increase on oxidative aging. Thus, the carboxylic acid and 2-quinolone types in an asphalt binder react irreversibly with the hydrated lime. Since hydrated lime is insoluble in the asphalt binder, this reaction removes these acidic components from the asphalt binder by adsorbing on the surface of the hydrated lime particles. The reactivity of hydrated lime with asphalt binder is highly dependent on binder crude source composition, with the more polar, high asphaltene-content asphalt binders generally being most responsive to the reactivity with hydrated lime [14-18]. The effect of adsorption of the asphalt binders' components containing carboxylic acid and 2-quinolone types on the physical properties of the remaining unabsorbed asphalt binder could be explained by the sample model shown in Fig. 1. In this figure both the carboxylic acid and 2-quinolone form hydrogen-bonded dimers and they also interact with each other to form a mixed dimer. Both the dimers and the mixed dimer show strong associations with asphalt binders by hydrogen bonds.

In a study of Branthaver [20] on an AAD-1 (contains high sulpher > 6% and high asphaltene) asphalt type, showed that 60% of the carboxylic acid and more than 90% of the 2-quinolone types were found in the so-called amphoteric fraction. The term amphoteric denotes asphalt binder components that have both acidic and basic chemical functional groups within the same molecule. Thus, these polyfunctional molecules can bind molecular agglomerates to form larger associations and bonds. These amphoterics play a major role in determining the rheological or physical properties of the asphalt binder, because the binder viscosity is directly related to the size of the agglomerated microstructural units [21]. The removal of the amphoteric fraction of the whole asphalt binder reduces the viscosity of the binder [20]. The addition of hydrated lime neutralizes the polar molecules strongly adsorbed onto the hydrated lime particles surface which prevents them from further reacting as a consequence of asphalt binder chemical aging phenomenon as





Fig. 1. Sample Model Illustrating Strong Hydrogen Bonding Interaction of Carboxylic Acids and 2-Quinolone Types in Asphalts (Based on a Study of Petersen [19]).

they are especially prone to aging, their removal generates an overall slower aging kinetics [13, 14, 22]. Neutralizing these polar molecules by hydrated lime also prevents their diffusion to the binder-aggregate interface and the remaining non-acidic surfactants of the asphalt binder can move to the binder-aggregate interface [7, 23]. Unlike the anionic surfactants, these surfactants are not easily displaced by water [5, 7]. This mechanism proposes the hydrated lime as an effective anti-stripping additive for the asphalt mixtures [24, 25].

The hydrated lime also offers an additional advantage due to its porosity nature. Hydrated lime has a dry porosity ranging from 60 to 70%, while other mineral fillers have values about 30-34% [26]. The higher porosity of the hydrated lime particles contributes to its overall porosity, while in case of a mineral filler, the porosity mainly comes from the voids between the particles. The porosity inside the particles sums up to the porosity between the particles leading to a much higher value of the hydrated lime. This could explain, at least partially, the effect of hydrated lime modification at higher and lower temperatures. The hydrated lime behaves similarly as classical fillers in terms of stiffening effect at a low temperature, while at a high temperature, the internal porosity of the hydrated lime particles is filled with asphalt binder in the matrix, therefore increasing the volume fraction (volume fraction of filler added to the asphalt binder) and hence, increasing the stiffening effect in comparison to the classical fillers [27, 28]. The volume fraction of the solid particles (i.e., fillers) govern the viscosity of a liquid [29, 30]. However, below room temperature, the asphalt binder-filled hydrated lime particles start to become deformable, and the mechanical contrast diminishes between matrix and inclusions, consequently, the system tends to behave as a function of the true volume fraction of solid instead of that of asphalt binder-filled hydrated lime particles.

Methodology

The hydroxyl group, O-H, of hydrated lime (RHL and NHL) as a reactive group with the asphalt binder was quantified using a developed method with the aid of the FTIR technique. The chemical interpretation of hydrated lime mechanism in asphalt binder was discussed based on the FTIR results and a literature support. Quantum chemical calculations also were used to support the experimental results. The subsequent sections explain the detailed methods followed to conduct the current research.

Preparation of Hydrated Lime-Modified Binders

The hydrated lime materials were used in the form of nanosize, NHL with particle sizes of 50-nm and 100-nm, and RHL. One original asphalt binder PG 58-28 from Gladstone, commonly used in Michigan was used throughout the current study. Hydrated lime materials (NHL and RHL) were applied at a rate of 20%, by the weight of asphalt binder which corresponding to 1.0% on the basis of the weight of the aggregate, as the commonly used dose in the field. The hydrated lime materials were mixed with the asphalt binder using a high-speed lab mixer. Mixing was done for 2 h at a rotational speed of 3,000 rpm and temperature of 130°C. A detailed description of all materials used and preparations can be found in

related studies [1, 2]. The study of the dispersion and deagglomeration of the NHL particles within the asphalt matrix is important before any testing proceeded, especially if higher percentages are used since the surface activity is a key aspect of the nanomaterials for the development of high-performance asphalt nanocomposite. The excessive agglomeration of the NHL particles within the matrix blocks particles surface area from contacting with other matter (i.e., asphalt binder) and hence lessen the possibility to utilize the full benefit of the nanomaterial [31]. In a related study [3], the energy dispersive x-ray spectroscopy technique was employed to visualize the dispersion extent and deagglomeration of the NHL particles within the asphalt binder matrix. Relying on the visual inference, the majority of the images showed a satisfactorily dispersion and deagglomeration of the NHL particles within the matrix.

Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transform infrared spectroscopy is a widespread method used to identify and quantify the amounts of known and unknown components in asphalt binders [32]. The asphalt binder's main functional groups can be quantified by using the FTIR technique. The main concept of the FTIR is based on the relation between the covalent bond of a molecule and the frequencies of infrared light. The infrared spectrometer sends an infrared radiation through a thin film asphalt binder sample guided through an interferometer and the transmitted radiation can be detected by a detector after passing through the sample. Based on the percentage of the transmitted radiation to the source radiation, the transmittance, reflectance, and absorbance can be obtained as a spectrum. The energy or the infrared radiation absorbed by the binder sample will cause the molecules to vibrate at different frequencies and the covalent bond of a molecule will vibrate based on the natural frequency of that bond. Absorption peaks from a spectrum represents a fingerprint corresponding to the frequencies of vibrations between the bonds of the molecules making up this material. Each material has a unique combination of molecules; therefore, no two compounds generate exact same infrared spectrum. The size of the peaks in a spectrum provides a positive identification (i.e., quantitative analysis) of the amount of material present.

Each chemical functional group has a unique natural frequency and a unique infrared spectrum. The peaks of the functional groups from the resulted spectrum can be compared with the infrared spectroscopy correlation table to recognize the main chemical functional groups generated in the asphalt binder. This method can be used to study both the effect of aging on the asphalt binder and the effect of different additives [33]. Scientists widely use the FTIR technique to analyze the modified asphalt binders. The chemical additives can change the chemical composition of the asphalt binder, consequently, the infrared spectrum of the binder will also change; therefore, the technique can provide a quantitative analysis of bonds generate [34].

To prepare the FTIR samples, the asphalt binders were heated at a temperature of 130°C, until the asphalt achieved a desired viscosity. A silicon slide plate with approximate dimensions of 15 mm long, 10 mm width, and 0.5 mm thickness was used to prepare the FTIR samples. A glass bar was used to pour a drop of the hot asphalt

binder on the silicon plate and another plate was used to distribute the sample to obtain a thin transparent film of the asphalt binder on the silicon plate. The amount of material required to prepare the FTIR samples is minimal, to provide reliable characterization of the components. The FTIR spectra were collected using a Jasco FTIR-4200 spectrometer. Because the need to be a relative scale for the absorption intensity, a background spectrum first was measured with no sample (i.e., silicon plate only) in the beam results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the asphalt binder sample only. A single background measurement can be used for many sample measurements as long as the instrument is still working because this spectrum is characteristic of the instrument itself. All spectra were recorded in a wavenumber length ranging from 500 to 4000 cm⁻¹ using 32 scans with a resolution of 4 cm⁻¹ (default spectra manager software settings).

Quantification of Hydroxyl Group

A quantitative analysis from the FTIR spectra requires some data processing with sophisticated mathematical methods to characterize the components of interest, which allows a more precise interpretation of them. In order to quantitatively estimate the O-H group in the studied hydrated lime (RHL and NHL)-modified samples, the FTIR spectrum at the chemical group peaks range was deconvoluted (Fig. 2), thus identifying the presence of various species by resolving overlapping peaks in the sample spectra and accordingly the areas under the curves were accurately calculated.

The following Gaussian function was used in peak fitting for the FTIR and Raman spectra:

$$y = a_{\circ} \exp\left[-(\ln 2) \cdot \left(\frac{x - a_1}{a_2}\right)^2\right]$$
(1)

where, a_1 , and a_2 are the peak height, center and HWHM (Half Width at Half-Maximum), respectively. Before peak deconvolution, the data were baseline corrected. The spline baseline was subtracted carefully considering the interfering factors that affect the shape of the spectrum. Following the baseline correction performed using linear interpolation and selection of zero values at minima in peak intensities, all spectra were corrected to zero [35, 36]. Then, the peak deconvolution using Gaussian peak fitting was applied to resolve the deconvoluted peaks. None of the peak parameters were preassigned in the fitting process. The iterations were stopped at the point where further iterations had no significant improvements in the goodness-of-fit expressed by χ^2 (the Weighted Sum of Squared Residuals, WSSR) and r^2 (the correlation coefficient) expressed as:

$$\chi^{2}(a) = \sum_{i=1}^{N} \left[\frac{y_{i} - y(x_{i};a)}{\sigma_{i}} \right]^{2} = \sum_{i=1}^{N} w_{i} [y_{i} - y(x_{i};a)]^{2}$$
(2)

$$r^{2} = 1 - \frac{\sum_{i} (y_{i} - f_{i})^{2}}{\sum_{i} (y_{i} - \overline{y})^{2}}$$
(3)

where σ , w, and f are the standard deviation, weight $(1/\sigma^2)$,



Fig. 2. Illustration Example of Peak Deconvolution for a Specific Range of Wavenumber.

and calculated y, respectively.

The peaks were deconvoluted using the fityk 0.9.8 software [37]. Finally, the relative abundance of chemical species (% area under curve) can be calculated accurately as follows:

$$Area(\%) = \frac{A_i}{\sum A_i} \times 100 \tag{4}$$

where A_i is the area of the compound under study.

It should be noted that ΣA_i is the summation of all deconvoluted areas under peaks of the entire spectrum (4000-500 cm⁻¹).

Quantum Chemical Calculations

Quantum chemical calculations can help explain experimental results. The two computational approaches used were an atom cluster approach using Gaussian basis functions, and an infinite slab approach using plane wave basis functions. Gaussian 09 [38] and Mopac 12 [39] were used for the atom clusters, and Quantum Espresso [40] was used for the infinite slab. The computed spectra [41] of hydrated lime was compared to experimental values. In addition both frontier orbitals and adsorption energies were compared for components such as saturate, napthalene, asphaltene, hydrated lime, and water.

Results and Discussion

The FTIR spectra (Absorbance vs. wavenumber mode) of the original asphalt binder and NHL (50-nm)-modified binder are shown in Fig. 3. The shown spectra are the average of two replicates for each binder type. The spike in the hydrated lime-modified asphalt binder spectrum (between wavenumbers of 4,000 and 3,500 cm⁻¹) is due to the presence of the hydroxyl group, O-H, in calcium hydroxide. The FTIR method explained before was employed to quantify the hydrated lime reactive group (hydroxyl group) within the modified asphalt binder. The area percent associated with each peak (Eq. (4)) was used to compare the hydroxyl group intensities of the hydrated lime (NHL and RHL)-modified asphalt binders. The FTIR calculations of the hydroxyl group are presented in Table 1.

The analysis of FTIR results shows the hydroxyl group of the hydrated lime at a wavenumber of approximately 3,642 cm⁻¹. It can also be seen that the NHL hydroxyl group affording values higher than that of the RHL. The FTIR investigation proves that the hydroxyl group of hydrated lime-modified asphalt is particle size dependent. More specifically, on a nanoscale, some physicochemical properties of hydrated lime can significantly differ from those of the bulk-structured material of the same chemical composition, which likely affect asphalt materials performance. The hydrated lime-asphalt binder interaction(s) are expected to increase due to the increase of hydrated lime specific surface-to-volume area. This conclusion is shared with that by Johansson [42]. Johansson stated that the potential interaction between RHL and asphalt binder is dependent on its rugose surface and very high specific surface area. Based on the FTIR analysis and consistently with the asphalt binder rheology results [1, 2], it is speculated that all hydrogen bonds contribute to a stiffness increase due to strong intermolecular forces between hydrogen bond donors, such as hydroxyl group presents in the hydrated lime, and hydrogen bond acceptors, such as carboxyl group presents in the asphalt binder. The high concentration of hydrogen bond donors results in strong intermolecular forces, which contribute to asphalt binder stiffness increase.

Decreasing hydrated lime particle size increases its specific surface area, increasing the adsorption of the components exist in the asphalt binder (i.e., concentration). Based on the previous studies [1, 2], the addition of NHL increased the stiffness of the asphalt binder as compared to the RHL. The amphoteric fraction of an asphalt binder containing the highly associated components is a major contributor to the asphaltene fraction and is primarily responsible for the elastic portion of complex shear modulus [20]. Thus, reducing the effects of this fraction by its partial removal from the asphalt through adsorption on the surface of the hydrated lime particle also should increase the viscous portion of the asphalt binder, yielding an asphalt binder phase that has a greater ability to dissipate shear stress through viscous flow. Logically, this contributes to an increase of the asphalt's ability to heal during repeated load cycling, thus increasing its resistance to



Fig. 3. FTIR Spectra of Original Binder and NHL (50-nm)-Modified Binder.

fatigue-induced damage [20].

Using plane wave basis functions (e.g. Ca.pz-hgh.UPF) and Quantum Espresso, the computed spectra of hydrated lime gave a primary peak of 3720 cm⁻¹, in reasonable agreement with the experimental values, above. Using Gaussian basis functions, a semi-empirical Mopac 12 calculation (at the PM7 level) gave slightly lower than experimental values, and an *ab initio* Gaussian 09 calculation (with hf/6-31g basis) gave values slightly higher than Quantum Espresso. Such calculations also yielded animations showing that the above and nearby peaks were associated with hydroxyl bond stretching and bending.

If adsorption of a ligand onto a substrate of hydrated lime (Fig. 4) was reasonably assumed to occur as follows, Substrate + Ligand => Substrate/Ligand Complex then the energy of adsorption (given as an enthalpy or heat of adsorption) is the energy of product minus reactants. In comparison to water (-960 kcal/mol), the ligands of a 22 carbon chain saturate, napthalene, and asphaltene had higher adsorption energies (~1040 - 1050 kcal/mol), confirming earlier observations that water cannot displace organic components from hydrated lime.

Adhesive or bonding processes that occurred between the hydrated lime substrate and the organic ligands were also amenable to frontier orbital (HOMO and LUMO) analysis. This analysis can predict bonding processes that occur when the electron acceptor's LUMO is energetically and geometrically accessible to the donor's HOMO. Thus relative reactivity and bonding propensity were given by the energy difference between the HOMO of one species and the LUMO of the other. A smaller distance or difference meant a larger reactivity. For example, the HOMO of water minus the LUMO of lime was 8.6 eV. When compared to napthalene, saturate, or asphaltene (differences of 4.5 to 5.0 eV), this indicated that water was the least reactive with hydrated lime. These results

Table 1. Hydroxyl Group Calculations for Hydrated Lime (NHL and RHL)-Modified Binders.

Sample	Position (cm ⁻¹)	Height	Area (%)	HWHM	χ^2	R^2
NHL(50-nm)	3642.42	0.932	3.46	15.6	9.72E-03	0.999
NHL (100-nm)	3642.52	0.801	2.03	15.3	1.06E-02	0.998
RHL	3642.06	0.434	0.702	14.9	1.06E-02	0.994

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Fig. 4. Computational Results of a Hydrated Lime Substrate Interacting with a Typical Asphaltene Ligand. (Light Gray, Hydrogen; Light Blue, Carbon; Dark Blue, Nitrogen; Red, Oxygen; Yellow; Sulfur; Medium Blue, Calcium Along Bottom of Hydrated Lime Substrate, Using VMD [43])

corresponded to water's lower energy of adsorption, above. In addition, napthalene, saturate, and asphaltene were more reactive with lime (differences above) than with each other (differences of 7.0 to 7.5 eV). Mopac 12 was used for the above adsorption energy and frontier orbital calculations.

Conclusions

This study first presented a state-of-the-art of the hydrated lime mechanisms in the asphalt-aggregate system based on previous studies on the RHL. In continuation of the authors prior studies on the newly fabricated NHL, a developed method with the aid of the FTIR technique was employed to quantify the hydrated lime reactive group (hydroxyl group) within the modified asphalt binder in an attempt to give an explanation of the interaction between hydrated lime (RHL and NHL) and the asphalt matrix. The use of the deconvolution method has made it possible to provide a reliable discussion of the FTIR results that were further supported by quantum chemical calculations. The analysis proved that the hydroxyl group of hydrated lime-modified asphalt binder is highly dependent on its particle size (i.e., surface-to-volume ratio). It is expected that the surface area of the hydrated lime particles is an effective factor in its interaction with the asphalt. The NHL-modified asphalt binder showed a higher hydroxyl group concentration as compared with the RHL. The hydrated lime-asphalt binder interaction may increase because of an increase in specific surface area (i.e., decrease of particle size). Generally stating, asphalts have more pronounced interaction with the NHL (50-nm) than 100-nm since the 50-nm particle-sized hydrated lime has a higher surface area as compared to the 100nm. Similarly, the RHL showed a lower hydroxyl group values as compared with the NHL (50-nm and 100-nm). Computed absorption spectra approximately matched experimental spectra, and computed energies of adsorption coupled with frontier orbital analysis helped describe hydrated lime's relative reactivity with water, saturate, napthalene, and asphaltene components.

Future Work

The current study presented an interpretation of the mechanism of the hydrated lime (RHL and NHL) in the asphalt binder from the FTIR point of view only; however, mechanisms remain difficult to be fully addressed without a precise knowledge with the aid of additional chemical investigations. In addition, since the current study is limited to one asphalt binder source only, more investigations can be conducted on a wide range of asphalt binders.

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