Physico-Chemical Characterization of Asphalt-Aggregate Interactions under the Influence of Freeze-Thaw Cycles

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ABSTRACT
Experiments were conducted to investigate the impact of different freeze-thaw cycling on the mechanical strength of eight different types of asphalt-aggregate mixtures. In these experiments, cylindrical specimens prepared by gyratory compactor were subjected to different freeze-thaw cycling. The indirect tensile strength at 25°C (77°F) was determined after different numbers of freeze-thaw cycles. All broken samples were contacted with cyclohexane to elute asphalt from the mixtures. Polar organic fractions were isolated from each of the mixtures using a solvent extraction method. It was observed that mild oxidation of asphalt results in recovery of large amounts (compared with unaged asphalts) of polar organics from the aggregate surface of all mixtures. Presumably these strongly bonded materials are important factors in protecting mixtures against the action of moisture. Test results also indicated that mixtures prepared from asphalt, which had been pre-aged, resisted freeze-thaw action more than unaged asphalt, and showed higher retained tensile strength than the unaged mixtures. In addition, results showed that mixtures prepared from dodecanophenone-treated asphalt interact with aggregates differently.

INTRODUCTION
Although considerable work has been done to try to understand the mechanisms directing the behavior of asphalt-aggregate mixtures in the presence of water, most of the emphasis has been placed either on empirical tests for measuring the physical strength (e.g., current Superpave® mixture design classified as TSR value) [1,2,3,4,5] or the influence of specific chemical components (functional groups) on the asphalt-aggregate bond [6,7,8,9,10,11,12]. A commonly reported difficulty is that tests are based on a pass-or-fail criterion. Unfortunately, the information obtained from the tests usually is too qualitative and field conditions are usually not simulated. Further, very little emphasis has been placed on the direct correlation of overall chemical composition with properties of asphalt-aggregate interfaces and physical properties of asphalt-aggregate mixtures. Empirical models developed previously do not explain adequately asphalt-aggregate interactions in the presence of water because they are not based on fundamental physico-chemical principles. The current Superpave® mixture design criteria for water stripping are based on empirical correlations with field data without consideration of the chemical interactions of asphalts with aggregates which affect pavement stability under the action of water. Additionally, the ability of asphalt-aggregate interfacial bonds to withstand exposure or weathering over extended periods of time has been studied minimally.

It has long been speculated that the adsorption and molecular orientation of asphalt molecules at the asphalt-aggregate interface region is a slow process and often continues for several hours or days even at high temperatures, depending on the composition of the asphalt binder and the nature of the aggregate surface. Obviously, the formation of the adsorbed layer may take longer at lower pavement temperatures because of the mobility effect. Therefore, it is important to understand how the loss of adhesive strength of mixes corresponds to the loss of certain chemical components that migrate to or from an aggregate surface as a function of time under the action of water.

It is the authors' speculation that the chemical and physical interactions that occur between asphalt and aggregate at the interface are influenced by freeze-thaw cycling over extended periods of time. Among these interactions affected by freeze-thaw cycling are those influencing adhesive strength. Water partially desorbs polar asphalt components from rock surfaces. The degree of desorption is a function of the asphalt-aggregate combination, the time in contact with water, the temperature of water, and the pH of the water. More specific and more speculative hypotheses proposed for this study are as follows. First, the greater the concentration of specific polar organics in asphalt (which in some cases can be determined by infrared spectroscopy), the more resistant asphalt-aggregate mixtures will be to water damage. It is speculated that bonding between polar organics in asphalts and rock surfaces is the major factor determining asphalt-aggregate bonding strength, and that moisture damage is related to the desorption of some of the polar organics. Second, water may disrupt binder cohesiveness as well as desorb polar organics from the rock surface. Third, the adhesive strength at the interface increases after mild oven aging. This is because the functional groups (especially ketones) formed during oxidation enhance adhesion and therefore mitigate moisture damage.

The objectives of this study are: 1) to establish a correlation between chemical properties and interactions that influence adhesion at asphalt-aggregate interfaces in the presence of water over extended periods of time, 2) to determine why the adhesive strength at the interface increases (or decreases) after short-term and long-term oven aging, 3) to investigate the effect of model compounds at the asphalt-aggregate interface in the presence of water over extended periods of time, and 4) to determine whether there is a common set of asphalt components at aggregate surfaces at the time of moisture damage failure.

EXPERIMENTAL DESIGN

One Strategic Highway Research Program (SHRP) asphalt, AAB-1, was selected for this study. Asphalt AAB-1 has relatively large amounts of sulfur (4.7%), nitrogen (0.6%), and oxygen (0.8%) and also has a high asphaltene content (17.3%) [13].

Two significantly different aggregates were used, a limestone and a granite. Limestone was obtained from the North Rawlins Quarry near Rawlins, Wyoming. Granite was taken from stockpiles at Granite Canyon Quarry near Cheyenne, Wyoming. Table 1a shows the sieve size gradation along with Wyoming DOT's specifications, which were used in this experiment. These two aggregates were chosen for study because of the differences in mineralogical composition and physical characteristics. The chemical properties of these two aggregates are also listed in Table 1a. As seen in Table 1a (bottom), the granite contains large amounts of silica, and therefore is classified as siliceous. The high percentage of calcium present in limestone classifies it as calcareous. These two different aggregates would be expected to show different chemical interactions with the various components of the asphalt. The variety and amount of other elements (aluminum, iron, magnesium, sodium, potassium) present in the aggregates would be expected to influence the chemistry of the adhesive bond between asphalt and aggregate as well as the sensitivity of that bond to water and temperature cycling.

The data presented subsequently are from eight different types of mixtures. They consist of neat asphalt AAB-1 mixed with limestone and granite, AAB-1 mixed with limestone and granite, then the mixture subjected to oven aging at 100°C (212°F) for 20 hours prior to making cylindrical specimens, AAB-1 pretreated with hydrated lime (20 mass % in the asphalt) and then mixed with limestone and granite, and AAB-1 pretreated with dodecanophenone (1 mass % in the asphalt) and then mixed with limestone and granite. Each mixture contains 60 grams asphalt and 1050 grams aggregate, so that the asphalt content of each mixture is approximately 5.5%. However, for lime-treated mixtures, an additional amount of asphalt (approximately 10 grams) was added into the lime-treated mixtures so that the total asphalt content is nearly 5.5%.

The 4-inch diameter by 2.5-inch high cylindrical specimens were prepared using a gyratory compactor. Bulk specific gravities and theoretical maximum specific gravities were measured to ensure that the air void content was approximately 7 percent. The deviation of air voids was limited to ±1 percent. Test procedures followed those used by the Wyoming Department of Transportation protocol. Two unconditioned (dry) and two conditioned (wet) specimens were tested for each mixture. Wet (conditioned) specimens were vacuum-saturated with distilled water so that 50 to 80 percent of their air voids were filled with water. Wet specimens then were subjected to successive freeze-thaw cycling to failure. One freeze-thaw cycle consists of freezing for 15 hours at –18°C (-0.4°F), followed by soaking in a 60°C (140°F) distilled water bath for 24 hours. The resilient modulus and indirect tensile strength were determined directly for the dry specimens and were determined for the wet (conditioned) specimens after various numbers of freeze-thaw cycles.

All broken (failed) samples were contacted with cyclohexane to remove the non-polar and intermediate polarity components of asphalt from the mixtures. When no more material was extracted by cyclohexane, a second extraction was performed using the mixed solvent of toluene-ethanol (9:1). This solvent extracts polar materials that were adsorbed onto aggregate particles. Solvent was removed from the extracts, and the polar components of the asphalts were weighed. Usually, they comprise under 10 mass percent of the original asphalt. Infrared (IR) spectroscopy was performed using PerkinElmer FT-IR spectrometer on solutions of these recovered polar materials in CS_2 to investigate how the polar materials in asphalts interact with aggregates before and after different numbers of freeze-thaw cycles. Infrared (IR) spectra of these residual materials show that they contain large amounts of polar functional groups compared with the original asphalts.

RESULTS AND DISCUSSION

Impact of Freeze-Thaw Cycles on Physical Properties of Mixtures

Table 1b lists the averaged tensile strength values of the unconditioned (control) and conditioned mixes. There is no significant difference between the mixtures that are prepared from the unaged AAB-1/limestone mixture and the moderately aged AAB-1/limestone mixture. Note that the mixtures prepared from lime-treated asphalt AAB-1 showed a lower average initial tensile strength than neat mixtures. This can be explained as follows. The addition of lime allows an increase in the optimum asphalt content used in the lime-treated mixes. It is believed that the additional asphalt content in the lime-treated mixes lowers the tensile strength. The tensile strength ratio (TSR), which is calculated as the ratio of conditioned indirect tensile strength to the dry indirect tensile strength, is used to characterize the stripping susceptibility of the mixture. The minimum TSR necessary to ensure good pavement performance has not yet been identified positively; however, a TSR of 0.8 after one freeze-thaw cycle is generally considered to be a reasonable minimum value under current Superpave® mix design criteria. Figure 1 shows the

tensile strength ratio (calculated from values in Table 1b) for specimens that were made from different types of mixtures after different freeze-thaw cycles. These mixtures include asphalt AAB-1 mixed with limestone, AAB-1 mixed with limestone and then oven aged at 100°C for 20 hours, lime-pretreated AAB-1 mixed with limestone, and dodecanophenone-pretreated AAB-1 mixed with limestone. It can be seen that the tensile strength ratio for all mixtures decreases as the number of freeze-thaw cycles increases. The decrease in the tensile strength ratio could be attributed to the loss of adhesion of the mixture and/or cohesion in the binder. Earlier studies [7,8] showed that some polar functional groups in asphalt that adhere to dry aggregate surfaces are easily displaced by water after freeze-thaw cycling. This displacement of asphalt components from rock surfaces by water could cause a reduction in the bonding between the aggregate and the asphalt. As seen from the figure, mixtures of unaged AAB-1 mixed with limestone aggregate (except for the dodecanophenone-treated sample) showed the greatest loss of TSR as a function of freeze-thaw cycles. The tensile strength ratio was quickly reduced to 0.8 after 2 freeze-thaw cycles and continued to decline to approximately 0.55 after 10 freeze-thaw cycles but at a slower rate. Mixtures made with AAB-1 pretreated with hydrated lime and limestone showed the least reduction in TSR. The tensile strength ratio remained above 0.8, which is the current minimum specification of the Wyoming Department of Transportation, after 15 freeze-thaw cycles. It was also observed that dodecanophenone-pretreated AAB-1-limestone specimens were more water sensitive than the controls. The tensile strength ratios of the dodecanophenone-modified mixtures are lower than those of the other mixtures after the same number of freeze-thaw cycles.

Figure 2 shows the same type of plot for specimens that were made from granite mixtures. It can be seen that only the lime-treated mixtures retain a reasonably high tensile strength ratio after ten freeze-thaw cycles. The mixtures prepared from asphalt AAB-1 mixed with granite, AAB-1 mixed with granite and then oven aged, and dodecanophenone-pretreated AAB-1 mixed with granite all failed after two freeze-thaw cycles. Failed in this case means that the specimens were broken prior to the determination of the tensile strength. Based on a limited number of data points, the tensile strength ratios for aged mixtures appear higher than those of unaged mixtures. The addition of 1% dodecanophenone to asphalt AAB-1 results in a higher tensile strength ratio after the same number of freeze-thaw cycles than the unaged asphalt, but this is due to low value for the unconditioned sample (Table 1b). The data for the lime-treated system show a lot of scatter, but the lime-treated mixtures prepared from siliceous aggregate are far more resistant to water damage than any other system examined.

The results shown in Figures 1 and 2 reconfirm past experience that both asphalt and aggregate composition play an important role in the moisture sensitivity of mixtures. The same asphalt mixed with different aggregates (limestone or granite) showed substantial differences in water-damage resistance after the same number of freeze-thaw cycles. The nature of the aggregate surface (chemistry or morphology) is also important to adhesion.

The beneficial effect of lime in reducing the moisture damage of mixtures is well recognized. Several mechanisms have been proposed to account for this beneficial effect. One mechanism proposes that compounds such as carboxylic acids form bonds with basic components of the rock. Unfortunately, carboxylic acids are readily displaced from mineral surfaces by water. Addition of lime to the aggregate surface neutralizes and ties up carboxylic acids so that they cannot interact with hydrogen bonding functionalities in the aggregate to produce moisture sensitive bonds. The results of the experiment described in the previous paragraph support this mechanism. The results are consistent with lime reacting with carboxylic acids, so that they do not form moisture sensitive bonds with the aggregate. Thus, more moisture resistant bonds with nitrogen-containing components from the asphalt form instead.

The improvement in moisture resistance from oxidative aging of the asphalt on the aggregate surface deserves further discussion. The mechanism by which aged materials improve moisture damage is still not well understood. However, two mechanisms are proposed here. One is the well-known phenomenon of increased viscosity due to oxidative aging. The other is that the change in asphalt composition from oxidation is a factor. It is well accepted that low temperature (<100°C) oxidation of asphalt results in the formation of polar, oxygen-containing functional groups. The interaction of these polar groups with the aggregate surface improves mixture resistance to moisture damage. This is demonstrated by the data in Figures 1 and 2 for mixtures prepared from the same asphalt (AAB-1) aged in contact with limestone (Figure 1) and granite (Figure 2) aggregates under the same conditions. The moisture resistance of AAB-1 on limestone seems to have been improved to a greater extent than on granite as a result of aging. This indicates that increased viscosity from oxidation cannot completely account for improvement in moisture-damage resistance. It is very likely that the polar functional groups formed during oxidative aging affect the adhesive interaction at the asphalt-aggregate interface. These polar functional groups formed on oxidation most likely interact with the aggregate bonding sites and alter the chemistry of the asphalt-aggregate bond, thus improving the moisture resistance of the mixture.

It is known that the principal products of oxidative aging of asphalts are aromatic ketones and aliphatic sulfoxides. Ketone formation may be more related to decreased moisture damage than sulfoxides for the following

reason. Ketones are generated from benzylic carbons that are part of polarizable aromatic ring systems and might also contain other polar heteroatom functionalities. This would produce polyfunctional molecules that are more polar than their precursors. These polyfunctional molecules would most likely be more resistant to water displacement from aggregates than single functional group sulfoxides. Sulfoxides are most likely formed from rather non-polar precursors, alkyl sulfides. If the results observed with this limited number of oxidatively aged asphalts prove to be a general trend, then mild aging should confer resistance to moisture damage. Usually, asphalts do not experience much age hardening until several years after pavements are laid down. This may explain early failure of pavements from moisture damage. Figure 3 is a schematic representation of various functional groups in asphalt, before and after oxidation, adhered to an aggregate surface.

Dodecanophenone was selected as a model compound to represent the ketone component in asphalt. It can be seen that addition of dodecanophenone to asphalt AAB-1 mixed with granite (Figure 2) appeared to reduce the moisture susceptibility of mixtures up to certain degree; however, the addition of dodecanophenone to asphalt AAB-1 mixed with limestone (Figure 1) reduced the moisture resistance of the mixture. Dodecanophenone, a single-ring benzylic ketone with a long side chain, probably is not representative of the ketones formed as a result of asphalt oxidative aging. Among other features, it is a small molecule compared with most asphalt components.

The results indicate that different aggregates might be expected to adsorb different amounts of polar material from the same asphalt, indicating that each asphalt-aggregate pair has unique interactions between active sites on the surface of the aggregate and reactive components from the asphalt. Different amounts of adsorbed asphalt components might be expected to be desorbed by water, again depending on aggregate type. Thus, the chemistry of the asphalt-aggregate interface determines the degree of water sensitivity of the asphalt-aggregate pair.

Impact of Freeze-Thaw Cycles on Chemical Properties of Mixtures

Polar organic fractions isolated from aggregate surface are a small part of the total asphalt in mixtures. As stated above, it is speculated that highly polar mineral surfaces attract the polar organic components of asphalts. Adhesion between these materials binds the mixture together. This bonding at the asphalt-aggregate interface may be affected by subjecting the mixture to freeze-thaw cycling. Figure 4 shows the weights of the polar organic fractions isolated from unconditioned (dry) mixtures of asphalt AAB-1 and the two aggregates and from the conditioned mixtures after freeze-thaw cycling. The number shown on the top of each bar indicates the number of freeze-thaw cycles that the sample had undergone. For example, unaged asphalt AAB-1 mixed with limestone had undergone six freeze-thaw cycles. Polar organic fractions were separated from the mixtures as described in the experimental section. Each sample has essentially the same amount of asphalt to begin with, so recoveries of various amounts of polar organics serve to differentiate each type of mixture. It can be seen that greater amounts of polar organics were recovered from the unconditioned (dry) limestone mixtures than from the equivalent granite mixtures, except for the dodecanophenone-spiked mixtures. As seen from the figure, the amounts of the polar organic fractions recovered from conditioned (wet) mixtures decreases after freeze-thaw cycling for the two unaged asphalt mixtures. This is consistent with earlier WRI studies that showed that water could displace certain adsorbed asphalt components from mineral surfaces [8]. However, the amounts of the recovered polar organic fractions increases after freeze-thaw cycling for the moderately aged and model compound-treated asphalt mixtures, the exception being the lime-treated asphalt coated on to limestone. This is consistent with the above speculation that oxidative aging generates materials that adsorb on aggregate surfaces and resist displacement by water.

Having examined the amounts of polar organics deposited on aggregates in these experiments, it is of interest to investigate the nature of individual compound types found in the polar organic fractions. Accordingly, IR spectra of the polar organic materials were obtained and quantitative estimations of amounts of specific compound types were calculated. Figure 5 shows a typical result from IR analysis of the polar organic fraction that was recovered from a mixture of 5 percent asphalt AAB-1 and granite, before and after freeze-thaw cycling. The carbonyl absorbance at ~1,700 cm^{-1} is of particular interest. The presence of this peak in an IR spectrum indicates that carboxylic acids and/or ketones are present. Because the asphalt has not been subjected to oxidative aging, it is assumed that the 1,700 cm^{-1} peak consists mostly of the former. The nearby 1,650 cm^{-1} peak is evidence for the presence of 2-quinolone types. Sulfoxides are identified by the distinctive peak at 1,030 cm^{-1}. This functional group is most easily formed in asphalt by mild oxidation, and is observed in unaged asphalts. These are the peaks of paramount interest in this study. Other features of note in the IR spectra are three peaks between 900 cm^{-1} and 700 cm^{-1}. These peaks are characteristic of aromatic molecules, which may be involved in interactions at asphalt-aggregate interfaces. The ketones formed by reaction with oxygen are largely aromatic. Ketones are the major oxygen-containing functional group formed during air oxidation of hydrocarbon components of asphalt, and their rate of formation is frequently used to indicate oxidation rate. Finally, the broad band over the range of 3,400 cm^{-1} to 3,000 cm^{-1} is a measure of the amount of hydrogen bonding in the sample. If there is a pronounced bulge over

baseline in this region, considerable hydrogen bonding interactions are taking place. This means that compounds such as phenols, carboxylic acids, pyrrolics, and 2-quinolones are interacting with one another and possibly other compounds such as sulfoxides. Hydrogen bonding interactions, which are comparatively strong, are characteristic of polar molecules and would be expected to contribute significantly to interactions between asphalts and aggregates. Hydrogen bonding also is an important interaction between water and polar molecules in asphalts (7). Both spectra in Figure 5 are characterized by fairly large bulges in the hydrogen bonding region.

Figure 6 shows the relative amounts of carbonyl compounds detected in polar organic fractions extracted from the various specimens using a polar solvent. The specimens first were soaked with cyclohexane, which dissolves most of the asphalt. Polar organic compounds that adhere to rock surfaces do not dissolve in cyclohexane. Instead, they are desorbed by the much stronger mixed solvent consisting of toluene-ethanol-water or, if adsorption is particularly strong, will remain on aggregate surfaces. Carbonyl compounds in asphalt tend to be relatively polar, and would be expected to become concentrated in the polar organic fractions. In unaged asphalts, carbonyl compounds consist for the most part of carboxylic acids. Upon aging, ketones and small amounts of additional acids are formed. These compounds are characterized by IR adsorption at approximately 1,700 cm^{-1}, and the height of this peak is measured in Figure 6.

Carbonyl concentrations in the polar organic fractions of unaged AAB-1 are not particularly large, whether or not the fractions were obtained from mixtures containing limestone or granite. Limestone appears to attract somewhat more carbonyl functionality than granite, as would be expected. One reason for the relatively low carbonyl content of these polar organic fractions is that AAB-1 does not contain large amounts of carboxylic acids, and the carbonyl content of an unaged asphalt would consist mostly of these organic acids. Freeze-thaw treatment also does not appear to alter carbonyl contents very much. There is a slight loss in the mixture of AAB-1 mixed with limestone.

The moderately aged materials contain some ketones, which are generated during oxidation. The carbonyl content of the polar organic fraction of the limestone mixture is much larger compared with that of the mixture of limestone with unaged AAB-1. Evidently the ketones formed during aging adsorb to the limestone surface. Freeze-thaw treatment results in a polar organic fraction with even more carbonyl content. These results contrast with those for polar organic fractions derived from mixtures of aged AAB-1 with granite. In this case either ketones were not generated, or were generated but were unadsorbed onto the granite surface, or were generated but were very strongly adsorbed. They do not appear in the polar organic fraction.

The dodecanophenone-treated samples are of interest. The amount of dodecanophenone in the mixture is large enough that its carbonyl adsorbance should be dominant compared with carbonyl compounds native to asphalt. In the limestone mixture, there is not a great deal of dodecanophenone in the polar organic fraction. Most of the dodecanophenone was either dissolved in cyclohexane (in which case it was not strongly adsorbed by limestone) or was so strongly adsorbed that the polar solvent did not desorb it. In contrast, the polar organic fraction obtained from the mixture of AAB-1 with granite shows strong evidence for the presence of the model compound. Such large carbonyl concentrations as seen in Figure 6 (bottom) are not observed in unaged asphalts. Also, carbonyl content is significantly reduced by freeze-thaw action. Obviously, the interaction of this model compound with the two aggregates is quite different.

The polar organics obtained from lime-treated samples are richer to some extent, in carbonyl compounds, than the untreated samples, particularly with the granite mixtures. The amount of polar organics also is larger (Figure 4), so lime is attracting carbonyl compounds. Freeze-thaw cycling results in loss of carbonyl compounds in the limestone mixtures, but not the granite mixtures. Perhaps this is one reason why lime improves granite mixtures with respect to water resistance.

The fact that carbonyl compounds can be desorbed from lime indicates that not all carboxylic acids (which should be the majority of the carbonyl compounds in an unaged asphalt) are chemically neutralized by lime (calcium hydroxide).

Figure 7 shows the IR results for sulfoxide-containing compounds strongly adsorbed onto the two aggregates. The limestone mixtures are at the top of the figure, and the granite mixtures are at the bottom of the figure. Like ketones, sulfoxides are products of oxidation. They are formed by the reaction of atmospheric oxygen with organic alkyl sulfides, which are native to petroleum. Sulfoxides form even under ambient conditions. Asphalts with large amounts of sulfur-containing compounds will produce significant amounts of sulfoxides on oxidation. AAB-1 is one such asphalt. Sulfoxides are weakly basic in character. It has been reported from previous studies that they do not bind as readily to aggregate surfaces as do carboxylic acids. However, previous model compound studies indicate that they are somewhat sensitive to displacement by water, but not as sensitive as carboxylic acids. Figure 7 shows some scatter with regard to sulfoxide content after freeze-thaw cycling. The possibility of sulfoxides being formed during sample work-up further complicates study of this functional group. It

is noteworthy that for the control samples (except those containing dodecanophenone) limestone adsorbed a larger amount of sulfoxides than granite. However, granite adsorbed a larger amount of the dodecanophenone-treated asphalt than the limestone. Also, the sulfoxides were more resistant to water displacement when coated on granite. It appears that the adsorptive behavior of asphalt functional groups on aggregate surfaces is complex.

The results shown in the above figures reconfirm past observations that demonstrate that both asphalt and aggregate composition play an important role in the moisture sensitivity of mixtures. On one hand, the chemistry of the asphalt with its strongly adsorbing component functionalities and its consequent adhesive behavior is important. On the other hand, the chemistry of the aggregate and how the different mineral components interact with the asphalt components are also important in characterizing the asphalt-aggregate interface.

CONCLUSIONS

Polar organic compounds of asphalts that adsorb on aggregate surfaces were isolated from eight mixtures. Each of the mixtures was exposed to freeze-thaw cycles for varying periods of time, up to 15 cycles in the TSR test. Polar organics were extracted from dry, freeze-thaw cycled mixtures. The polar organics were weighed and were studied by IR spectrometry. The composition of each mixture determined the amount of polar organics that were isolated.

Current specification for neat asphalt implies that there is a simple uncomplicated relationship between the binder characteristics and the performance of the asphalt mixture, and therefore the interactions between aggregate and asphalt are common, regardless of source of either component. This study clearly shows that there exists a specific interaction between an asphalt and a given aggregate in a mixture. The results show that there is not a common set of asphalt components at the aggregate surface at the time of moisture damage failure. Due to the interactions, an interfacial layer is created in most cases and its properties are different from neighboring phases. Thus it would be very difficult to establish general relationships between properties of an asphalt binder and the performance of an asphalt mixture, which would not depend on the type/nature of the asphalt-aggregate combination.

The study has confirmed an earlier study made by Plancher [8] and Petersen [9] concluding that some functional groups in asphalt that adhered onto aggregate surfaces appear to be rapidly displaced from aggregate surfaces by water after different cycles to equilibrium levels. The IR spectra of the recovered polar organics show that sulfoxides functional groups do not appear to be as greatly affected by water. Carboxylic acids are displaced by water, whereas ketone functional groups are not. Since sulfoxides and ketones are generated in asphalts by reaction with oxygen, intentional mild aging might protect asphalt concrete against moisture damage.

Aging of asphalt generates a different class of polar molecules, and these appear to be protective against the debonding action of water. TSR retained strength as shown by the freeze-thaw cycles. Generally, the aged mixtures were more resistant to water damage than the unaged mixtures. However, mixtures prepared with the model ketone performed poorly in the TSR test. This suggests that the ketones formed upon oxidation of asphalt contain other components (other functional groups) that promote adhesion. Some of the compounds formed as a result of aging adsorb very strongly on aggregate surfaces, and appear to protect against freeze-thaw action.

It is recommended that more fundamental studies be conducted on the physico-chemical characteristics of asphalt-aggregate mixtures. In particular, the impact of freeze-thaw cycling on these characteristics could lead to a better understanding of the mechanism of the asphalt-aggregate interaction. It is believed that the identification and characterization of the functional types normally present in asphalt or formed on oxidative aging of asphalt, which influence molecular interactions, afford a fundamental approach to relating asphalt composition to asphalt properties and, thus, the performance of asphalt-aggregate mixtures.

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LIST OF TABLES AND FIGURES

TABLE 1a Gradation along with WYDOT Specification and Compositional Properties of Limestone and Granite Aggregates

TABLE 1b Indirect Tensile Strength of Several Mixtures before and after Successive Freeze-Thaw Cycles

FIGURE 1 Impact of freeze-thaw cycles on the tensile strength ratio of several mixtures of AAB-1 (modified) coated on limestone.

FIGURE 2 Impact of freeze-thaw cycles on the tensile strength ratio of several mixtures of AAB-1 (modified) coated on granite.

FIGURE 3 Schematic representation of neat asphalt and oxidized asphalt components adhering to aggregate at the asphalt-aggregate interfacial region.

FIGURE 4 Amount of the polar organic fraction extracted from treated and untreated AAB-1 mixed with limestone (top) and granite (bottom) before and after freeze-thaw cycling.

FIGURE 5 IR results of moderately aged AAB-1 mixed with granite before and after freeze-thaw cycling.

FIGURE 6 Infrared results for carbonyls extracted from aggregate for treated and untreated AAB-1 mixed with limestone (top) and granite (bottom) before and after freeze-thaw cycling.

FIGURE 7 Infrared results for sulfoxides extracted from aggregate for treated and untreated AAB-1 mixed with limestone (top) and granite (bottom) before and after freeze-thaw cycling.

TABLE 1 (a) Gradation along with WYDOT Specification and Compositional Properties of Limestone and Granite Aggregates

Gradation

Sieve Size	Limestone	WYDOT Spec.	Granite	WYDOT Spec.
25 mm	100	100	100	100
19.0 mm	99	90 ~ 100	100	100
12.5 mm	83	55 ~ 90	94	90 ~ 100
9.5 mm	67	45 ~ 85	82	60 ~ 85
4.75 mm	47	30 ~ 65	42	40 ~ 60
2.36 mm	28	20 ~ 50	30	25 ~ 45
1.18 mm	16	---	22	---
0.06 mm	10	5 ~ 30	16	10 ~ 30
0.03 mm	7	---	12	---
0.015 mm	5	---	9	---
0.0075 mm	4.1	2 ~ 7	6.1	2 ~ 7

Composition

Sample	Limestone	Granite
Acid Insoluble		
Al_2O_3, %	0.34	13.95
SiO_2, %	9.36	65.55
Total, %	**9.7**	**79.50**
Acid Soluble		
$CaCO_3$, %	74.58	3.62
Fe_2O_3, %	0.37	5.61
MgO, %	11.24	1.09
Na_2O,%	N/A	3.42
K_2O, %	N/A	5.64
Total, %	**86.19**	**10.32**
Total of minor & trace elements, %	4.11	10.18

TABLE 1 (b) Indirect Tensile Strength of Several Mixtures before and after Successive Freeze-Thaw Cycles

	Indirect tensile strength, psi								
	0 cycle	1 cycle	2 cycles	4 cycles	6 cycles	8 cycles	10 cycles	12 cycles	15 cycles
AAB-1/Limestone	85.6	73.2	67.2	51.0	43.2	---	45.0	Failed	
AAB-1/Limestone, aged	87.0	83.1	80.5	76.6	59.8	53.5	---	53.7	Failed
Lime-treated AAB-1/Limestone	75.9	68.5	68.2	69.6	64.6	57.5	67.5	---	61.4
Dodecanophenone-treated AAB-1/ Limestone	84.1	70.5	---	45.1	36.7	Failed			
AAB-1/Granite	83.1	66.6	42.8	Failed					
AAB-1/Granite, aged	90.9	76.6	53.2	Failed					
Lime-treated AAB-1/Granite	70.2	67.9	67.2	55.8	69.1	57.5	64.9	Failed	
Dodecanophenone-treated AAB-1/ Granite	61.0	57.5	41.2	Failed					

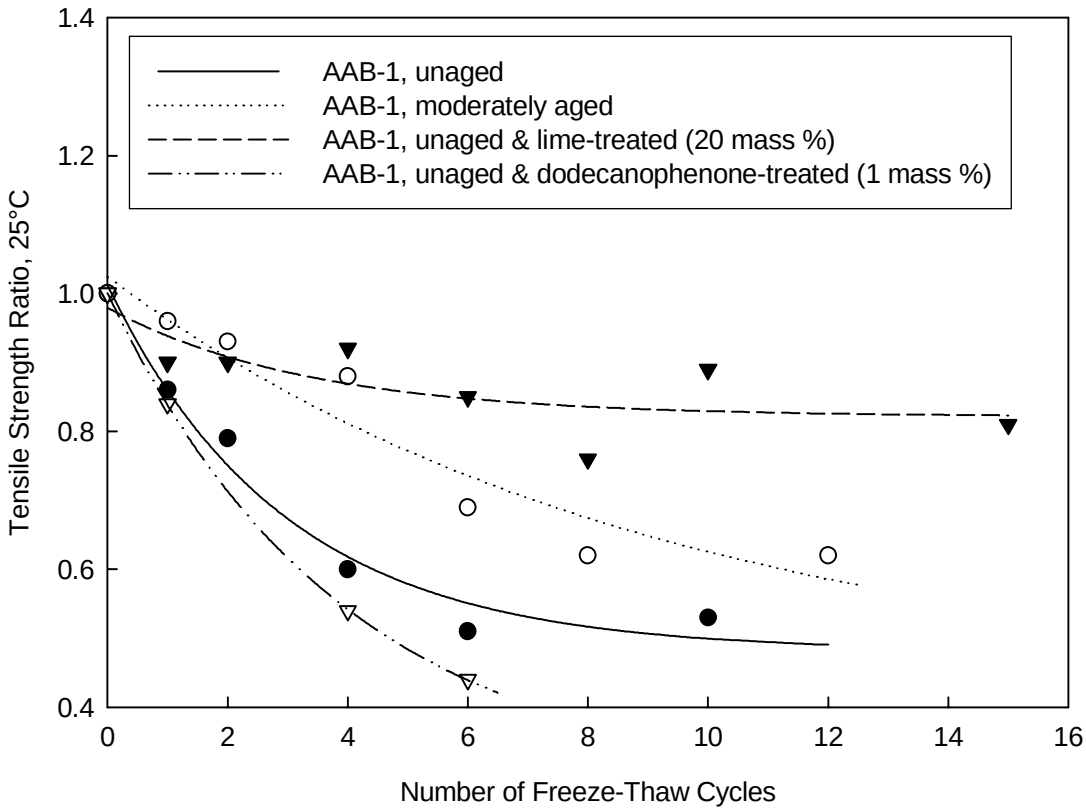

FIGURE 1 Impact of freeze-thaw cycles on the tensile strength ratio of several mixtures of AAB-1 (modified) coated on limestone.

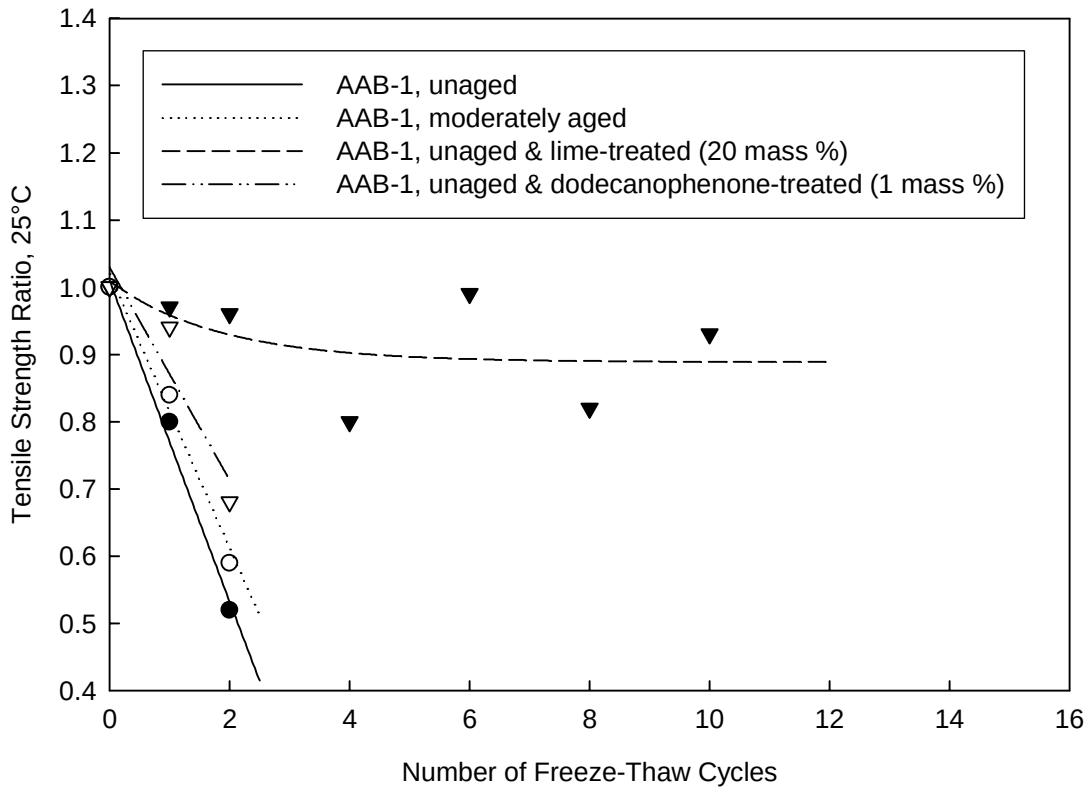

FIGURE 2 Impact of freeze-thaw cycles on the tensile strength ratio of several mixtures of AAB-1 (modified) coated on granite.

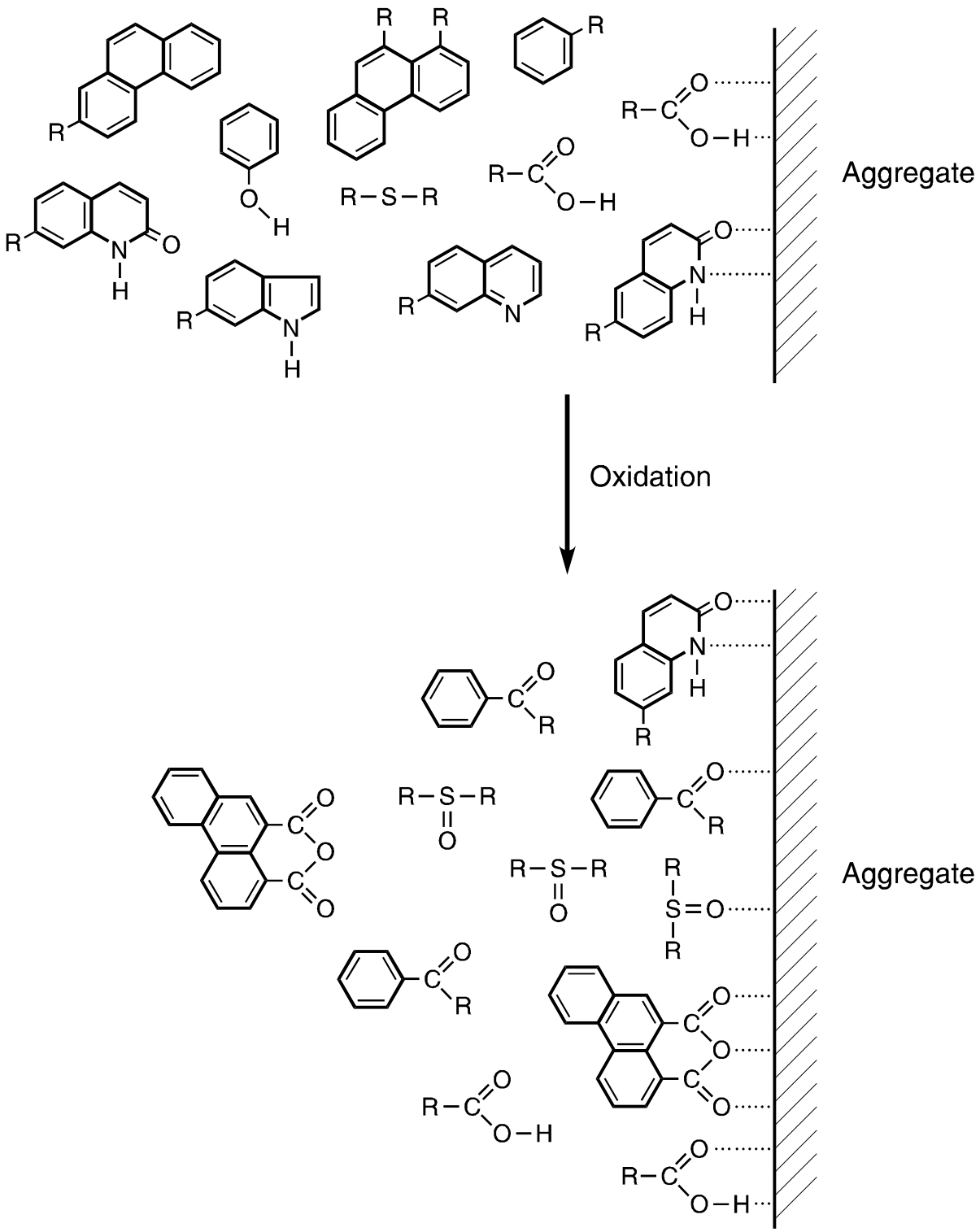

FIGURE 3 Schematic representation of neat asphalt and oxidized asphalt components adhering to aggregate at the asphalt-aggregate interfacial region.

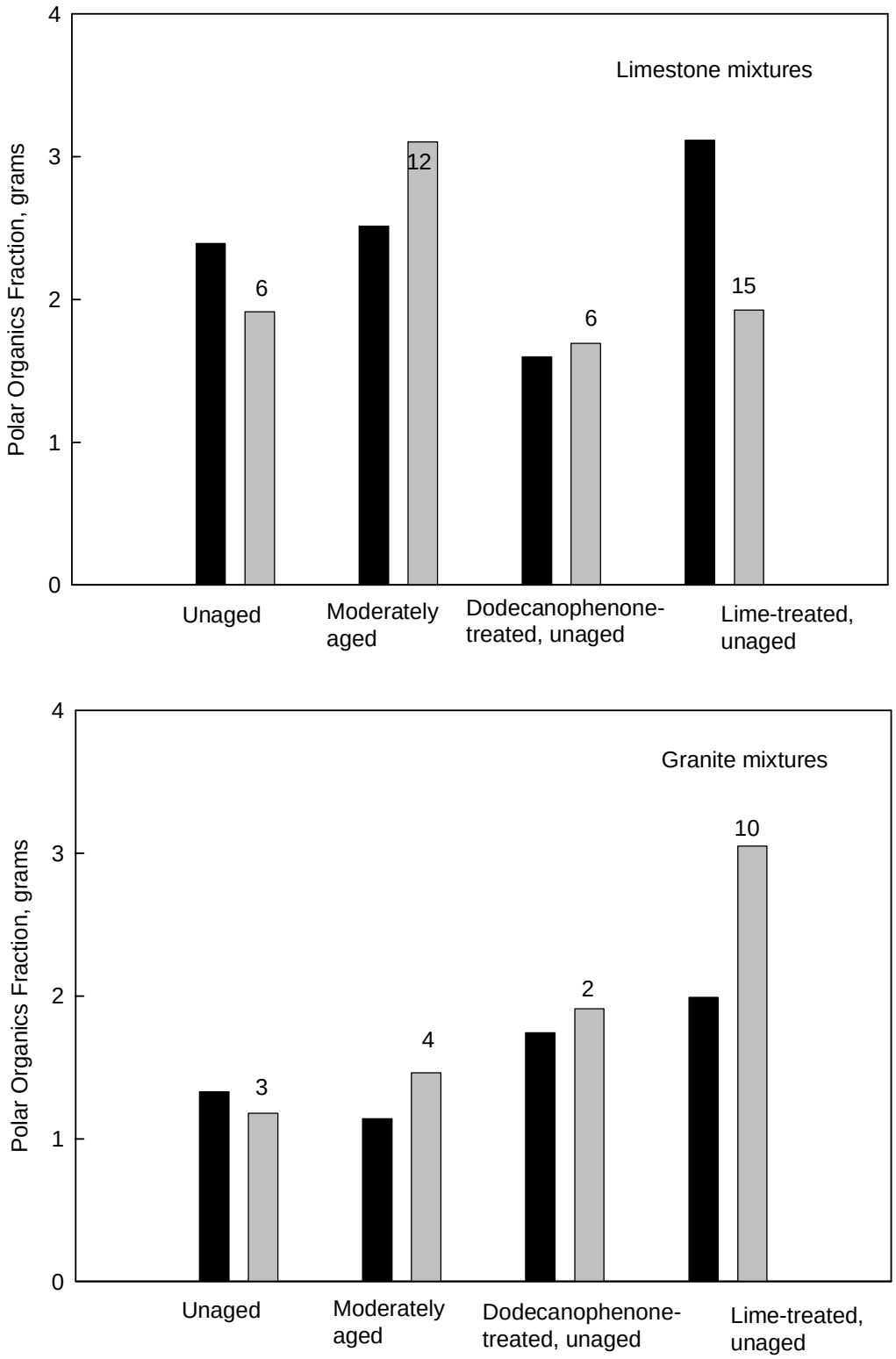

FIGURE 4 Amount of the polar organic fraction extracted from treated and untreated AAB-1 mixed with limestone (top) and granite (bottom) before and after freeze-thaw cycling.

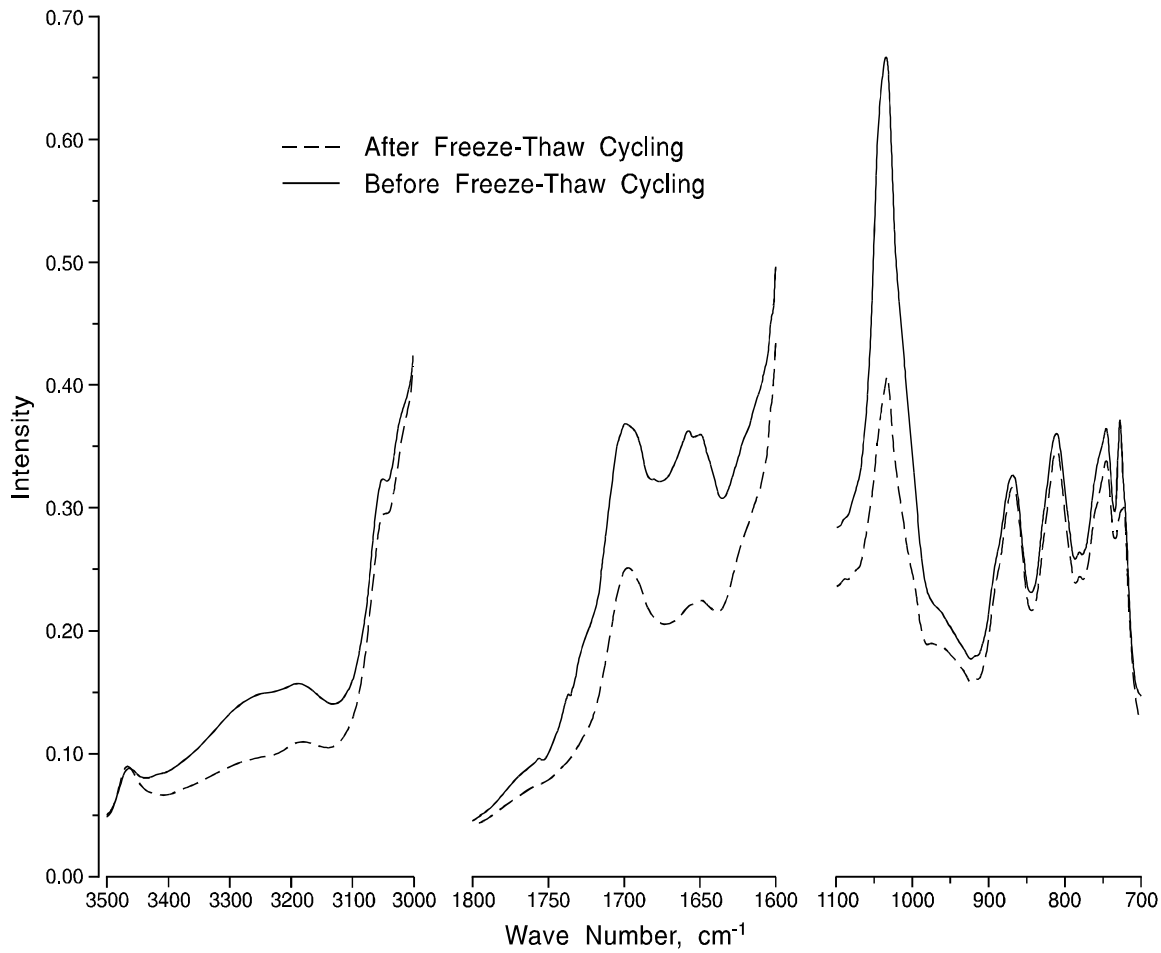

FIGURE 5 IR results of moderately aged AAB-1 mixed with granite before and after freeze-thaw cycling.

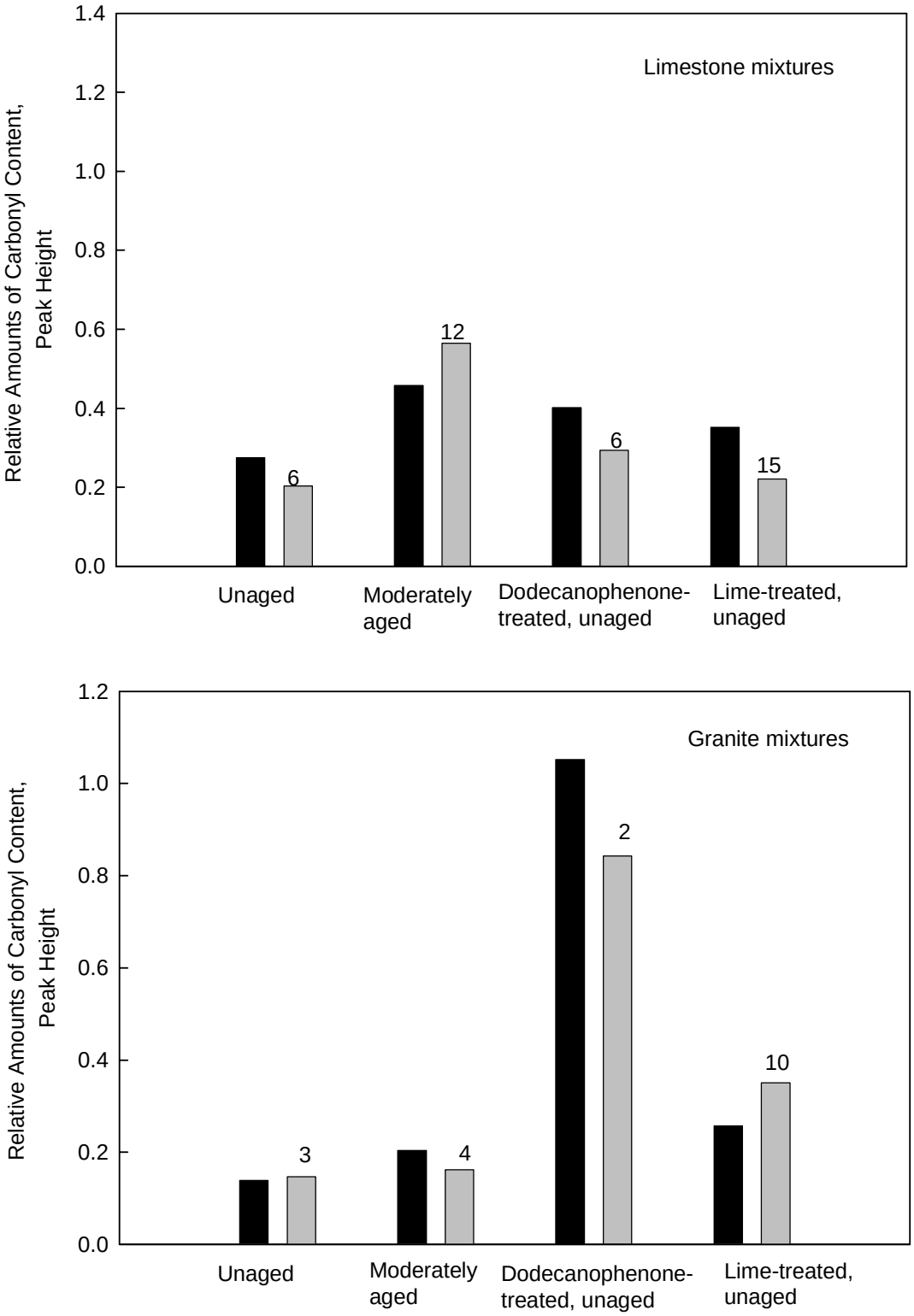

FIGURE 6 Infrared results for carbonyls extracted from aggregate for treated and untreated AAB-1 mixed with limestone (top) and granite (bottom) before and after freeze-thaw cycling.

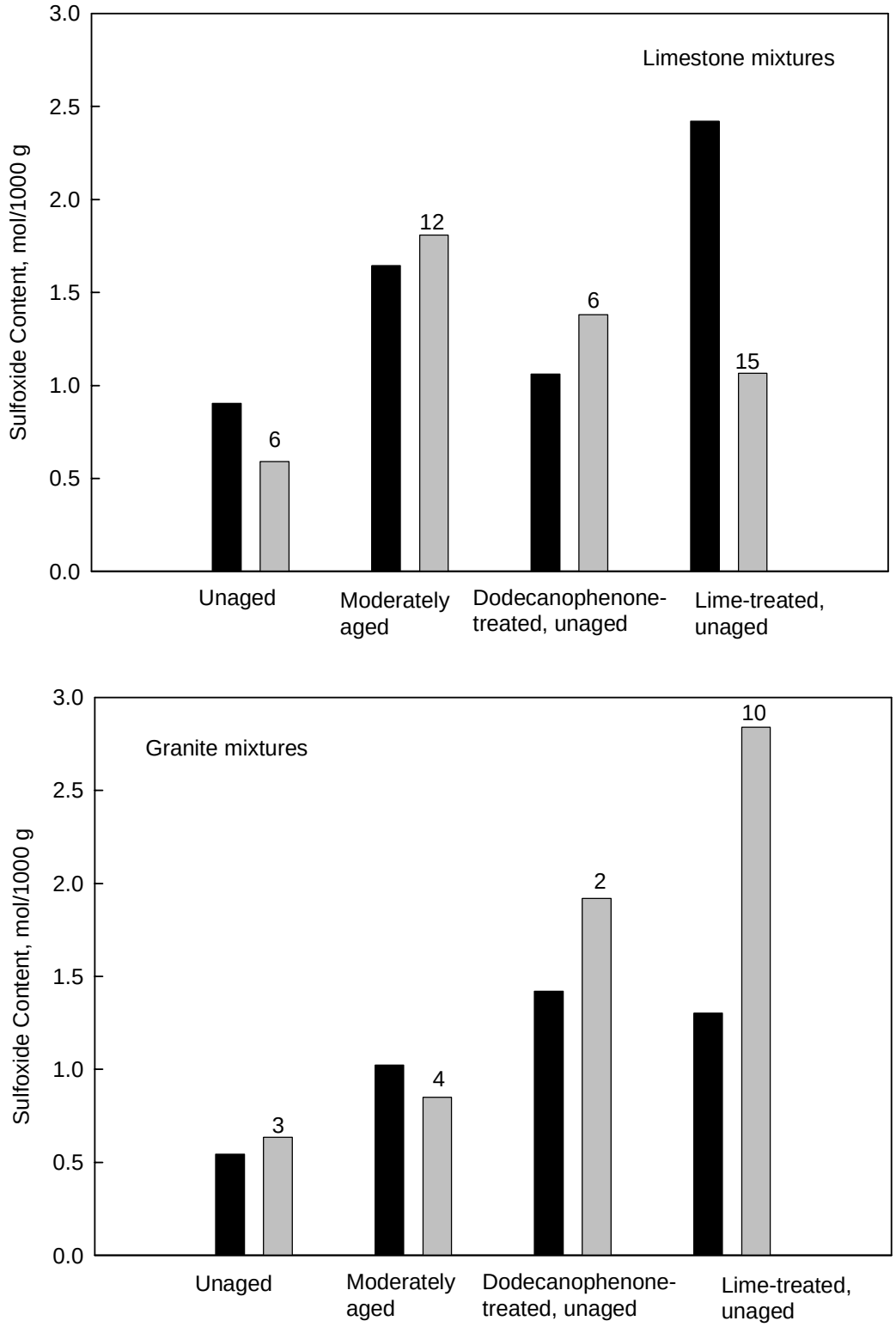

FIGURE 7 Infrared results for sulfoxides extracted from aggregate for treated and untreated AAB-1 mixed with limestone (top) and granite (bottom) before and after freeze-thaw cycling.