Technical White Paper

# Impact of Water on Aging

## Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 07

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## Technical White Paper

# IMPACT OF WATER ON AGING

### Summary

Atmospheric pressure aging experiments were conducted to determine whether the presence of moisture during aging has any significant influence on the aging kinetics. The results, based on the aging of five SHRP asphalts, show that there is no significant influence at atmospheric pressure.

### Statement of Problem

It has been well recognized that the major cause of the long term hardening of asphalt binder in pavements is the chemical reaction with atmospheric oxygen. This slow reaction is controlled by the intrinsic reactivity of the asphalts, the temperature regime at the pavement surface, and the rate of diffusion of oxygen into the binder films in the interior of the surfacing.

Many attempts have been made to simulate road aging in the laboratory, but most have been met with marginal success. One reason is that the different causes of road failure, like heavy traffic or poor construction, obscure the affect of the asphalt binder. Some other major factors include improper laboratory aging environments (exceedingly high oven temperatures) as well as failure to account for environmental conditions like relative humidity. Furthermore, there is very little investigation of the chemical composition and structure changes during oxidative aging in the presence of water.

Recent research [Thomas 2002; Huang et al. 2008] has shown that the presence of moisture increases the rate at which aging progresses in laboratory experiments using the pressurized aging vessel (PAV). In these experiments, several SHRP asphalt binders were first aged using the standard procedure of the rolling thin film oven (RTFO) test (AASHTO T240). The RTFO-aged asphalts were then further aged using the PAV test (AASHTO PP1) at lower temperature of 80°C for different durations, ranging from 144 hours, 240 hours And 480 hours. For the samples that were aged in the presence of water, a glass Petri dish containing 15 mL of water was included in the pressure vessel. The partial pressure of water in the pressure vessel was calculated to be 0.047 MPa at 80°C.

Unaged and aged samples in both dry and moist conditions were subjected to chemical and rheological analysis. The rheological properties of the RTFO- and RTFO/PAV-aged asphalt binders were studied as a function of oxidative aging time and the presence or absence of water. The results indicated that PAV aging in the presence of water accelerated the aging process. The average stiffness increase for all asphalts is approximately 18.1% due to the presence of water in PAV, based on rheological data from eight SHRP asphalts. The average carbonyl content increase is approximately 12.9% due to the presence of water in the PAV. The results suggest that water disrupts the colloidal structure of asphalt molecules during the pressurized oxidative aging process [Thomas 2002; Huang et al. 2008]. Figure 1 shows the average stiffness increase for all asphalts. The average increase is approximately 18.1% due to the presence of water in PAV, based on rheological data from eight asphalts. Figure 2 shows the average carbonyl content increase of approximately 12.9% due to the presence of water in PAV. The aging shift factor used in the paper is considered to be modulus (stiffness) changes with respect to the modulus at the reference aging time, and give an indication of how the rheological properties of a material change with aging time. The details can be found in Huang et al. [2008].

Henry's law suggests that at 1 atmosphere this effect may be 20 times smaller and perhaps insignificant. This research aims to answer the question of whether or not moisture significantly affects oxidation rates in binder films at temperatures and pressures occurring in real pavement situations. Since aging ultimately leads to embrittlement and pavement failure, determining whether the accelerated aging occurs at atmospheric pressure is important to the prediction of pavement performance.

## Goal

The goal of this experiment is to evaluate the impact of water on the long-term aging characteristics of asphalts at atmosphere pressure. More specifically, the objective is to correlate the rheological properties to the chemical properties of asphalts after long-term aging in the presence and absence of water at 1 atmosphere pressure and pavement service temperature, 60C. Because the physical properties of asphalt are controlled by the interactions of the molecules from which it is composed, an understanding of these interactions should provide the basis for understanding its physical behavior and thus its durability.

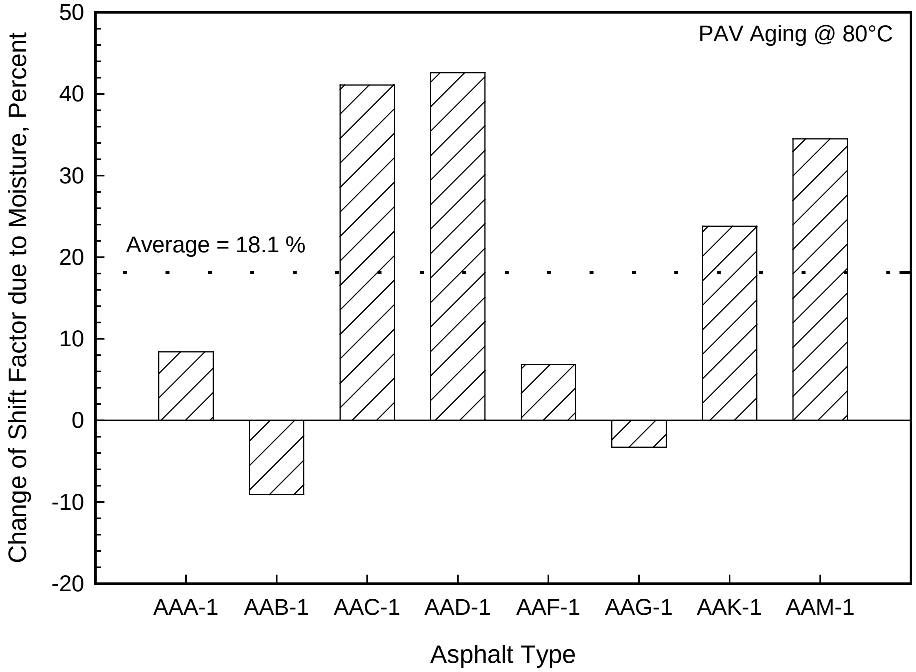

Figure 1. Impact of water in change of physical property during PAV aging.

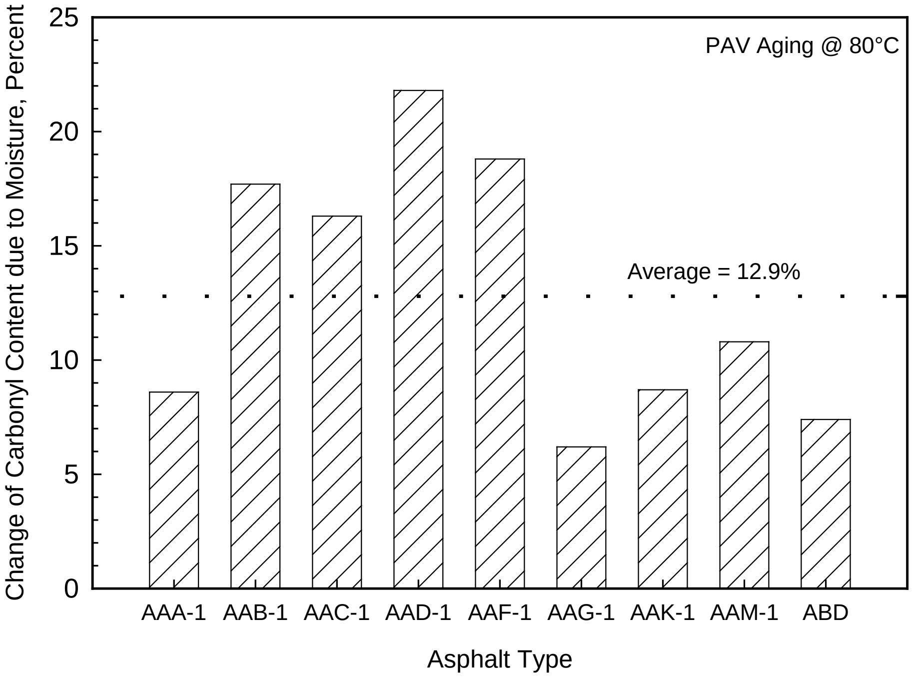

Figure 2. Impact of water in change of chemical property during PAV aging.

The sensitivity of asphalts to environmental factors were determined using a laboratory, force-draft oven at ambient pressure and pavement service temperature to age unmodified asphalts in the presence and absence of moisture in the oven. Analytical testing included spectroscopic and rheologic analyses of the aged materials.

## Support of FHWA Strategic Goals

The ability to reliably reproduce in-service pavement aging in the laboratory is vital to the highway community. With the development of a correlation between laboratory aging data and field pavement performance, it may be possible to predict the advent of distresses in the field, therefore, improving the cost effectiveness of the preventive maintenance and/or rehabilitation measures that are commonly used. This subtask supports the FHWA Strategic Goal of Optimizing Pavement Performance

## Experimental Design

Five SHRP asphalts (AAB-1, AAC-1, AAD-1, AAM-1, and ABD) were prepared for thin film (100 microns) aging at ambient pressure and 60°C for different durations in dry conditions. Aging in presence of water was conducted at 60C for the same durations as those of dry conditions. For the samples that were aged in the presence of water, a dish containing 2800 mL of water was included in the oven. This is the only difference between what is defined as dry and a moist-aging experiment. A humidity monitor was used to check the humidity of the oven when water is partial- (700 ml-over the weekend) and full-filled (2800 ml) conditions. It was observed that the oven has 99% humidity regardless of full- or partial-filled conditions.

Aged, thin film samples were removed from the oven and were subjected to IR and rheology testing. The concentrations of carbonyl and sulfoxide were determined using a Perkin Elmer Spectrum 1 infrared spectrometer. The infrared spectrum of an asphalt sample was obtained by dissolving 50 mg of asphalt in 1 mL of carbon disulfide, placing the sample in a sodium chloride cell with a 0.1-cm path length, and recording the spectrum, using solvent compensation, from 4000 to 600 $cm^{-1}$. The amount of the carbonyl-containing compounds, centered at 1700 $cm^{-1}$ (1680 ~ 1720 $cm^{-1}$) was estimated using a peak-height method. The concentration of sulfoxide-containing compounds, centered at 1030 $cm^{-1}$(1020~1050 $cm^{-1}$) was determined by measuring the area under the peak. The area was then converted to moles per liter by multiplying by the dilution factor, in this case 21, and dividing by the cell path length, 0.1 cm, and the absorptivity coefficient (4900 L/mole $cm^2$). The absorptivity coefficient was determined from the analysis of several model compounds that contain the sulfoxide functional group and is described in reference [Petersen 1981; 1986]. These infrared tests were used to investigate if aging in the presence of 99% of humidity at 1 atmospheric pressure affects the chemical properties of asphalt binders. If significant moisture-induced aging had occurred, rheological analyses would have been conducted.

## Results and Discussions

That asphalt reacts with atmospheric oxygen, which stiffens or hardens the asphalt, has been recognized for more than 75 years. The change in the amounts of fractional components of asphalt generally seen on oxidative aging is a movement of components from the more nonpolar to the more polar fractions.

Asphalt is believed to be a dispersion of strongly associated, immobilized polar molecules in a solvating solution composed of less polar asphalt molecules. Because of molecular association, polar oxidation products greatly alter the state of dispersion of asphalt components, therefore changing the mobility and thus, the chemical reactivity of asphalt molecules susceptible to oxidation.

Of particular relevance to asphalt oxidation is the sensitivity of the associated components to dissociation on temperature increase and the location of molecules within the associated components that are potentially reactive through oxygen. As temperature increases, weakly associated molecules in the extremities of the structured components are mobilized into the asphalt solvent phase. Because molecular mobility greatly accelerates the oxidation reactions, the location within the microstructure of the precursors to the major oxidation products, carbonyls and sulfoxides, greatly influences precursor reactivity. Since carbonyl and sulfoxide are two main products generated from oxidative aging, this project mainly focuses only on how aging in the absence and presence of water influences the chemical properties of asphalt binders.

Figures 3 through 7 show carbonyl (1680~1720 $cm^{-1}$) peak heights as a function of aging times in oven at different aging temperatures for aged samples in dry conditions. A little bit of scattering in the data is observed. However, it appears that aging temperatures of 40°C and 50°C do not cause significant oxidative aging as compared to aging temperatures of 60°C and 70°C regardless of asphalt type.

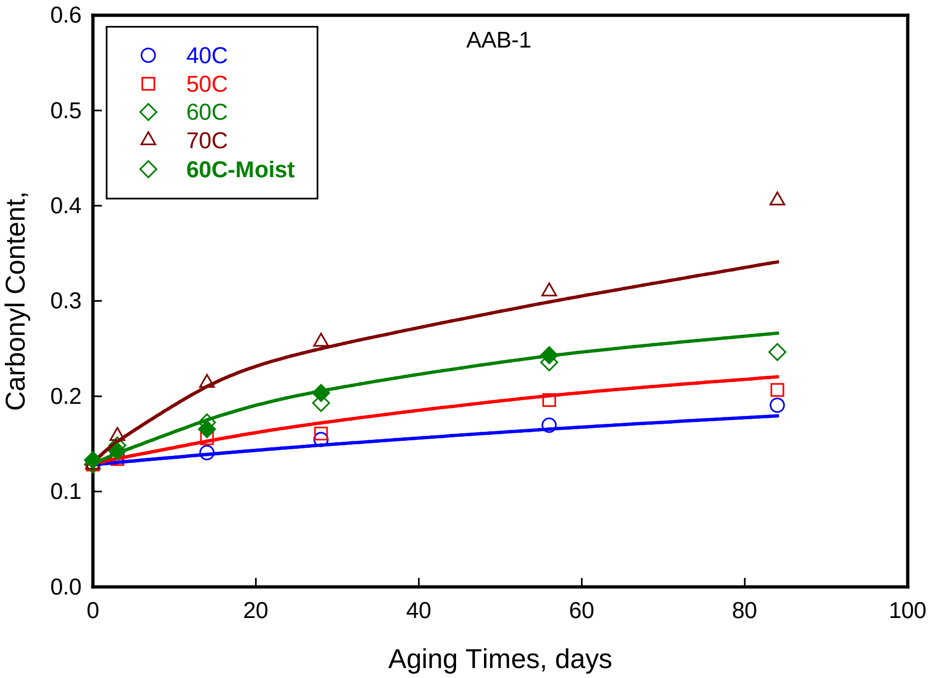

Figure 3. Carbonyl content for asphalt AAB-1 aged at ambient pressure at different aging temperatures for different durations.

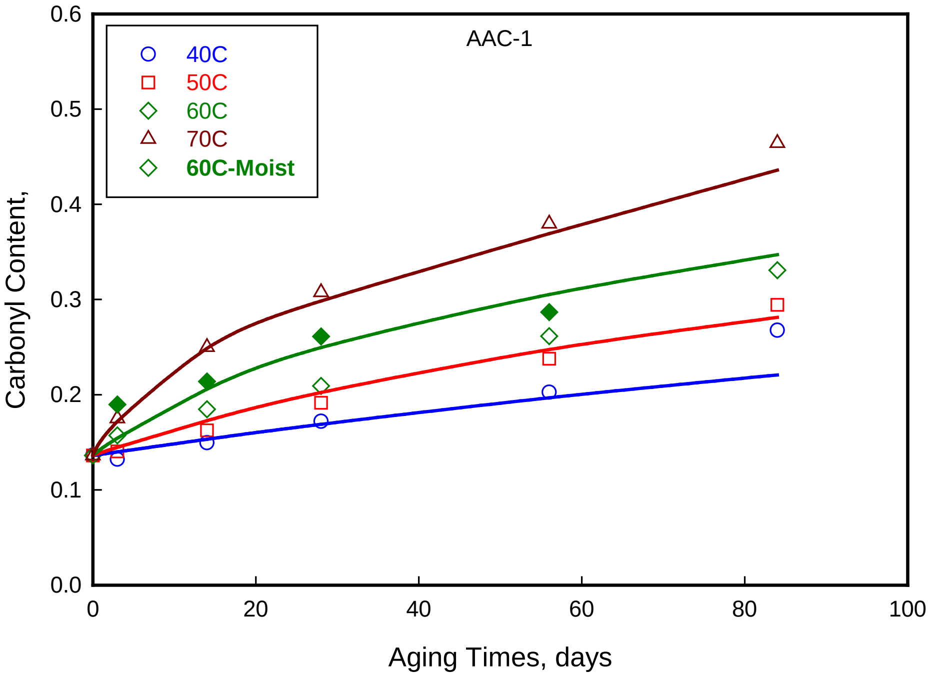

Figure 4. Carbonyl content for asphalt AAC-1 aged at ambient pressure at different aging temperatures for different durations.

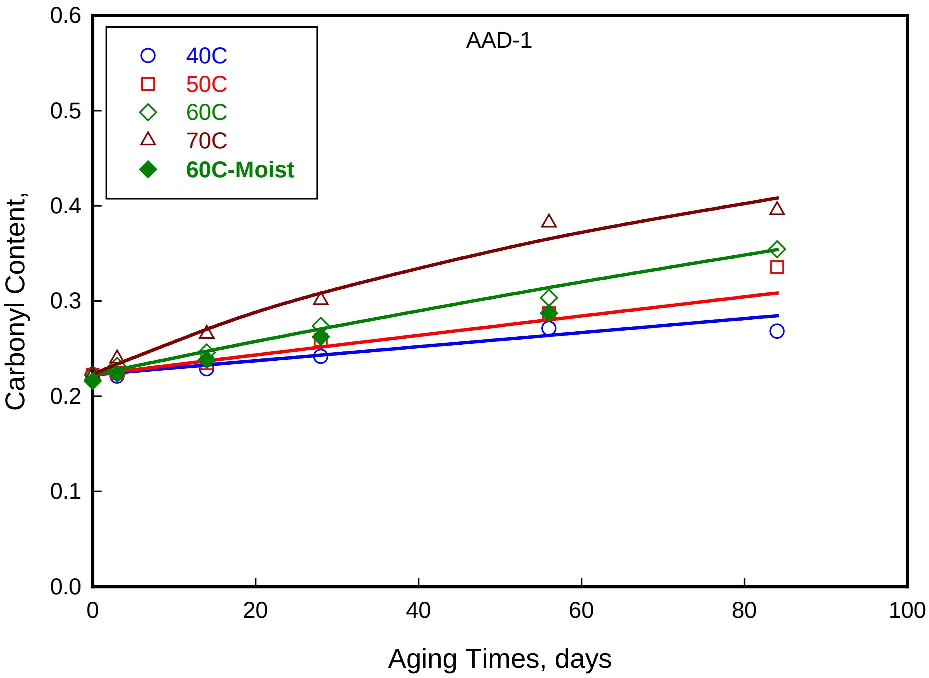

Figure 5. Carbonyl content for asphalt AAD-1 aged at ambient pressure at different aging temperatures for different durations.

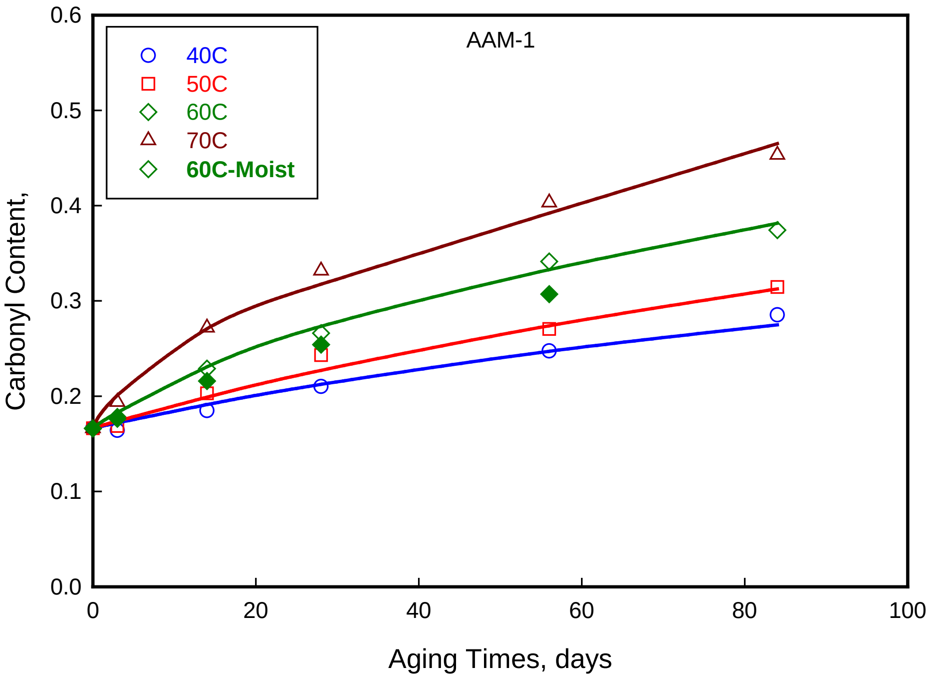

Figure 6. Carbonyl content for asphalt AAM-1 aged at ambient pressure at different aging temperatures for different durations.

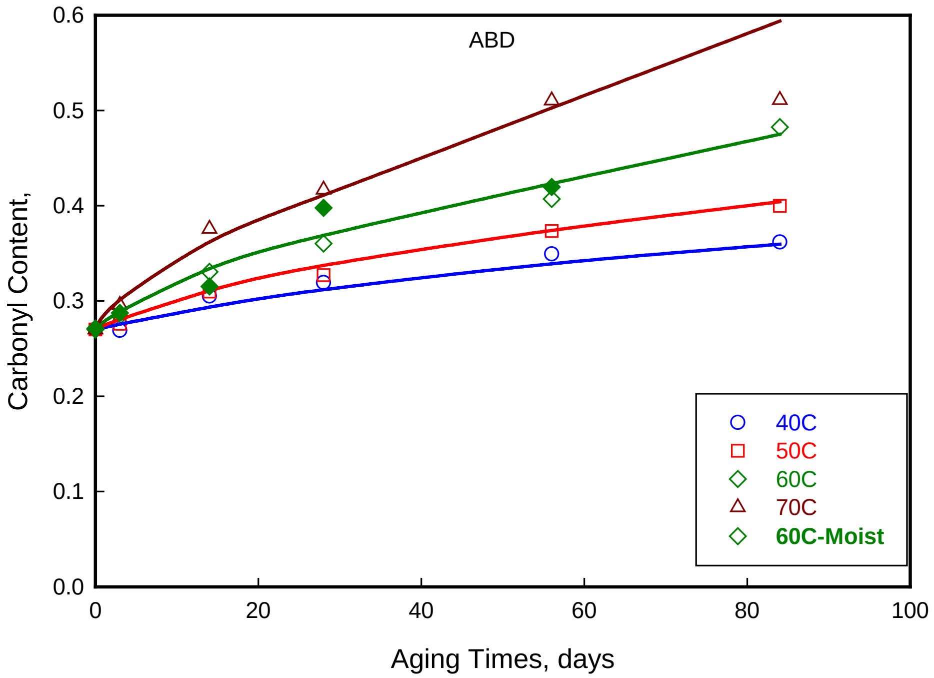

Figure 7. Carbonyl content for asphalt ABD aged at ambient pressure at different aging temperatures for different durations.

To verify if typical aging kinetic model works on IR results, a typical first-order and zero-order aging kinetic model (or Glover's aging kinetic model) was applied to curve fit all sets of the IR results. The equations used are as follows [Glover, 2010]:

$$C_P = M * \left[1 - \exp^{(-k_1 * t)}\right] + K_2 * t$$

$$S_P = M * \left[1 - \exp^{(-k_1 * t)}\right] + K_2 * t$$

Where Cp and Sp are carbonyl and sulfoxide peak heights formed in asphalt, respectively, $k_1$ and $k_2$ are reaction constants for the fast reaction (first order) and the constant reaction (zero order), respectively. M is the total carbonyl (or sulfoxide) produced in the fast reaction.

Figure 3 shows carbonyl plot for asphalt AAB-1that is aged at 40°, 50°, 60°, and 70°C for different durations along with fitted curves. Glover's aging kinetic model fits very well on the measured data points. This figure demonstrates the rapid increase of carbonyl content as aging time increases initially and then the slower rate after the initial jump. High aging temperature (70°C) dominates the observation. Figures 4 through 7 show the same types of plot for asphalts AAC-1, AAD-1, AAM-1, and ABD, respectively. These figures indicate that different asphalts show different chemical changes for similar amounts of oxidation. Figures 8 through 12 show sulfoxide plots for asphalts AAB-1, AAC-1, AAD-1, AAM-1, and ABD, respectively. The same phenomenon observed in carbonyl also occurs on sulfoxide formation. Again, different asphalts react differently with the same amounts of oxidation. Tables 1 and 2 show the calculated reaction constants of $k_1$ and $k_2$ for carbonyl and sulfoxide formations, respectively. For carbonyl formation, it can be seen from Figures 3 through 7 that asphalt AAD-1 changes the least regardless aging temperatures. On the other hand, asphalt ABD changes the most within different aging temperatures. For sulfoxide formation, asphalt AAM-1 changes the least at any aging temperatures. And, asphalt AAD-1 changes the most regardless the aging temperatures. It is well known that the oxidation rate coefficients are strongly dependent on temperature. The typical Arrhenius equation was used to plot the relationship between reaction constants ($k_1$ and $k_2$) and the reciprocal of absolute aging temperatures. The Arrhenius equation is expressed as:

$$K(T) = A\exp^{(-E_{act}/RT)}$$

Where K is reaction rate coefficient, A is frequency (or pre-exponential) factor, $E_{act}$ is activation energy, R is gas constant, and T is absolute temperature. Note that the activation energy can be thought of as the amount of energy which must be supplied to the reactants in order to react with each other.

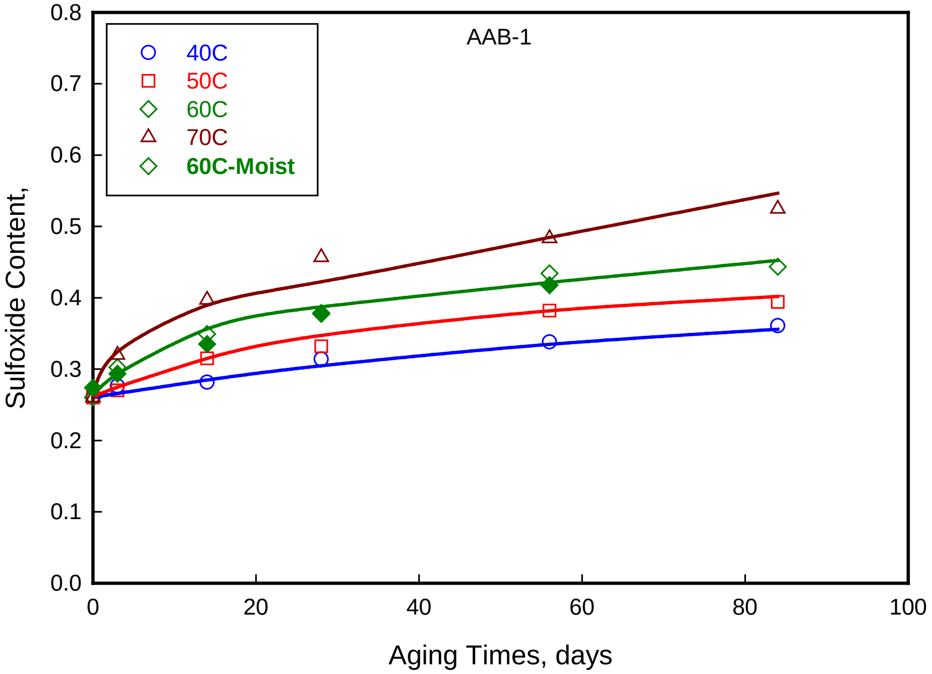

Figure 8. Sulfoxide content for asphalt AAB-1 aged at ambient pressure at different aging temperatures for different durations.

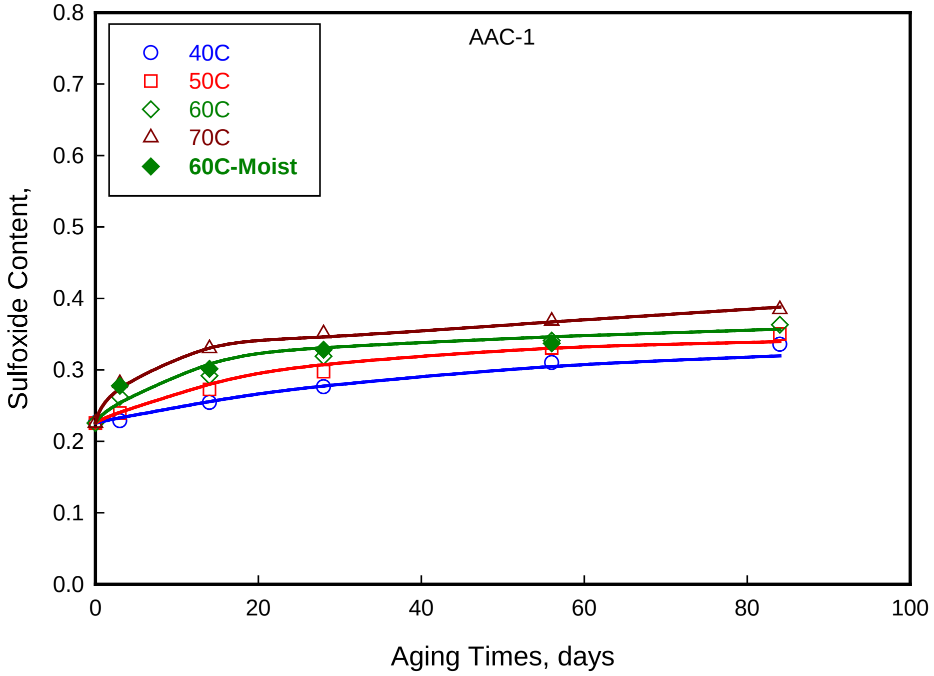

Figure 9. Sulfoxide content for asphalt AAC-1 aged at ambient pressure at different aging temperatures for different durations.

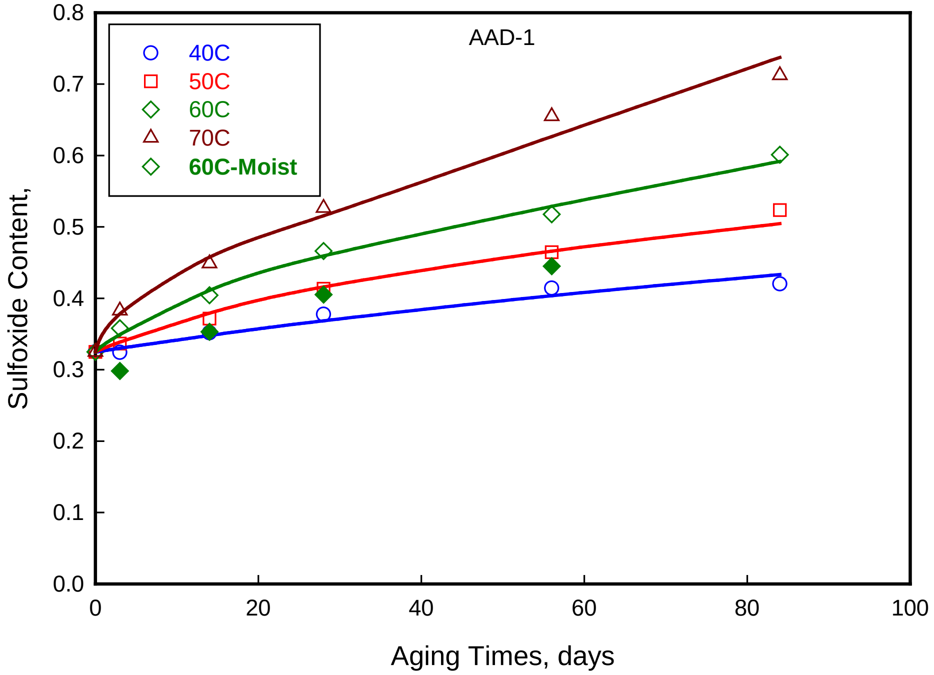

Figure 10. Sulfoxide content for asphalt AAD-1 aged at ambient pressure at different aging temperatures for different durations.

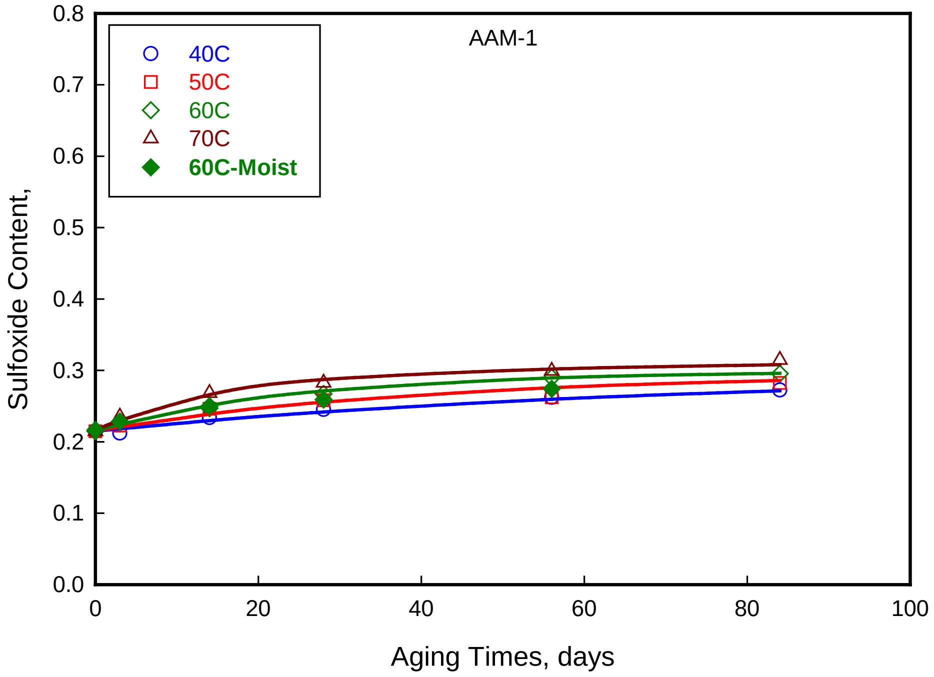

Figure 11. Sulfoxide content for asphalt AAM-1 aged at ambient pressure at different aging temperatures for different durations.

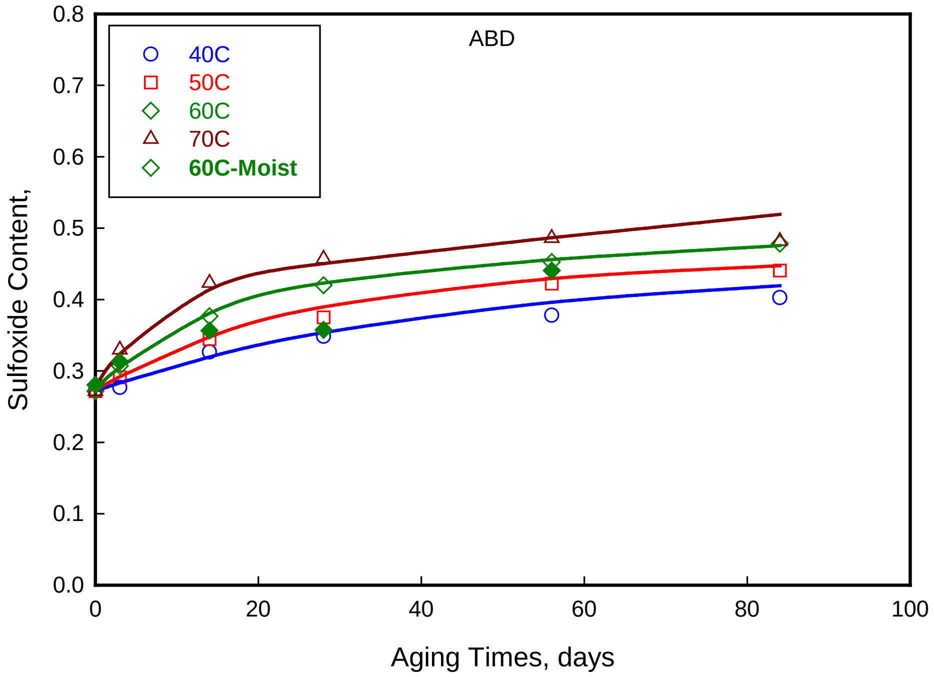

Figure 12. Sulfoxide content for asphalt ABD aged at ambient pressure at different aging temperatures for different durations.

Table 1. Reaction coefficients for carbonyl absorbance versus aging times for different asphalts at different aging temperatures.

| Asphalt | ln $k_1$ | ln $k_2$ | 1/T |
|---|---|---|---|
| AAB-1 | -4.82949 | -9.29271 | 0.003193 |
| | -3.9989 | -8.31119 | 0.003095 |
| | -3.21818 | -7.3886 | 0.003002 |
| | -2.48295 | -6.51978 | 0.002914 |
| | **Y=-8405.1X+22.011** | **Y=-9932.4X+22.45** | |
| AAC-1 | -4.71639 | -7.87908 | 0.003193 |
| | -3.82125 | -7.2287 | 0.003095 |
| | -2.97985 | -6.61737 | 0.003002 |
| | -2.18749 | -6.04166 | 0.002914 |
| | **Y=-9058.3X+24.21** | **Y=-6581.5X+13.138** | |
| AAD-1 | -7.27297 | -7.31588 | 0.003193 |
| | -6.00195 | -7.1596 | 0.003095 |
| | -4.80723 | -7.01271 | 0.003002 |
| | -3.68215 | -6.87438 | 0.002914 |
| | **Y=-12862X+33.8** | **Y=-1581.4X-2.2659** | |
| AAM-1 | -4.08882 | -7.46674 | 0.003193 |
| | -3.95124 | -6.93025 | 0.003095 |
| | -2.94685 | -6.42596 | 0.003002 |
| | -2.001 | -5.95107 | 0.002914 |
| | **Y=-7752X+20.404** | **Y=-5429X+9.87** | |
| ABD | -3.58935 | -7.54468 | 0.003193 |
| | -2.91916 | -6.9013 | 0.003095 |
| | -2.2892 | -6.29655 | 0.003002 |
| | -1.69595 | -5.72704 | 0.002914 |
| | **Y=-6782X+18.068** | **Y=-6510.6X+13.246** | |

Table 2. Reaction coefficients for sulfoxide absorbance versus aging times for different asphalts at different aging temperatures.

| Asphalt | $\ln k_1$ | $\ln k_2$ | 1/T |
|---|---|---|---|
| AAB-1 | -4.07643 | -8.35972 | 0.003193 |
|  | -3.08013 | -7.56413 | 0.003095 |
|  | -2.14364 | -6.81629 | 0.003002 |
|  | -1.26174 | -6.11204 | 0.002914 |
|  | **Y=-10082X+28.119** | **Y=-8051X+17.35** |  |
| AAC-1 | -3.71676 | -9.39525 | 0.003193 |
|  | -2.96096 | -8.62238 | 0.003095 |
|  | -2.25053 | -7.89614 | 0.003002 |
|  | -1.5815 | -7.21198 | 0.002914 |
|  | **Y=-7648.3X+20.707** | **Y=-7820.1X+15.577** |  |
| AAD-1 | -4.26866 | -7.36868 | 0.003193 |
|  | -3.10397 | -6.71825 | 0.003095 |
|  | -2.48823 | -6.10773 | 0.003002 |
|  | -1.41616 | -5.53195 | 0.002914 |
|  | **Y=-9858.5X+27.258** | **Y=-6578.4X-13.639** |  |
| AAM-1 | -4.22918 | -13.019 | 0.003193 |
|  | -3.68735 | -11.5052 | 0.003095 |
|  | -3.17805 | -10.0823 | 0.003002 |
|  | -2.69844 | -8.74228 | 0.002914 |
|  | **Y=-5483X+13.28** | **Y=-15319X+35.9** |  |
| ABD | -3.65841 | -8.64056 | 0.003193 |
|  | -3.08427 | -7.97404 | 0.003095 |
|  | -2.54459 | --7.34773 | 0.003002 |
|  | -2.03637 | -6.75774 | 0.002914 |
|  | **Y=-5810X+14.895** | **Y=-6743.9X+12.895** |  |

Figures 13 through 16 show the reaction constants as a function of the reciprocal of absolute aging temperatures for all five asphalts for both carbonyl and sulfoxide formations. It can be seen that for the initial (rapid) carbonyl formation, the reaction rate of asphalt AAD-1 is more sensitive to the aging temperatures than the other four asphalts. However, after the initial spurt, the reaction rate of asphalt AAD-1 becomes more stable than the other four asphalts. For sulfoxide formation, it can be seen that all five asphalts do show similar sensitivity on the reaction rate to aging temperatures at initial reaction rate. However, after the initial spurt, the reaction rate of asphalt AAM-1 shows the most sensitivity to aging temperature than the others. The linear equations are also listed in Tables 1 and 2 for different asphalts in terms of carbonyl and sulfoxide formations. The slope (-E/R) of each equation can be represented as activation energy after multiplying by a gas constant value.

As mentioned in the experiment section that the moist aging was conducted only at 60°C for the same time durations as those of dry conditions. The carbonyl and sulfide formation as a function of aging times are also included in Figures 3 through 12 for different asphalts. The hollow symbols represent dry conditions and solid symbols represent moist aging at 60°C for different aging times. It can be seen that moist aging does not change significantly in terms of the change of carbonyl and sulfoxide formations.

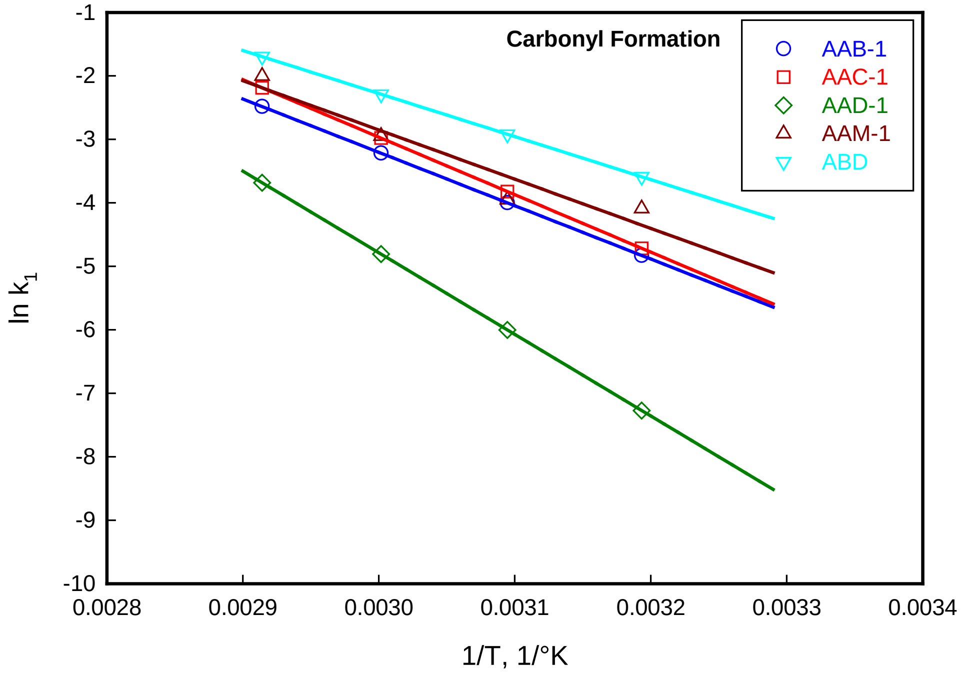

Figure 13. Fast reaction rate coefficient versus reciprocal absolute aging temperature for carbonyl formation.

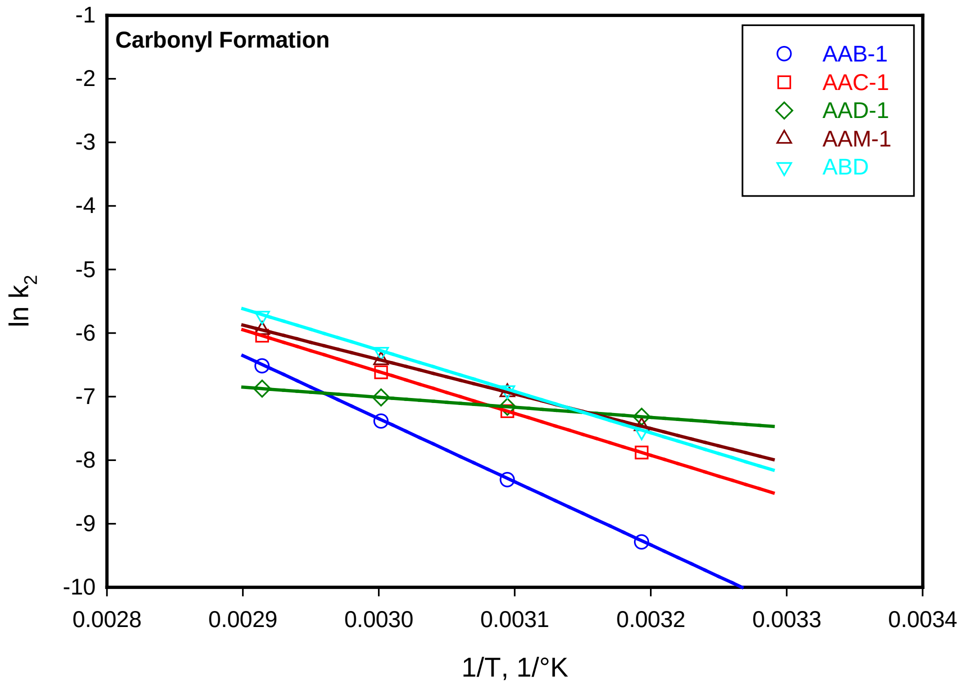

Figure 14. Constant reaction rate coefficient versus reciprocal absolute aging temperature for carbonyl formation.

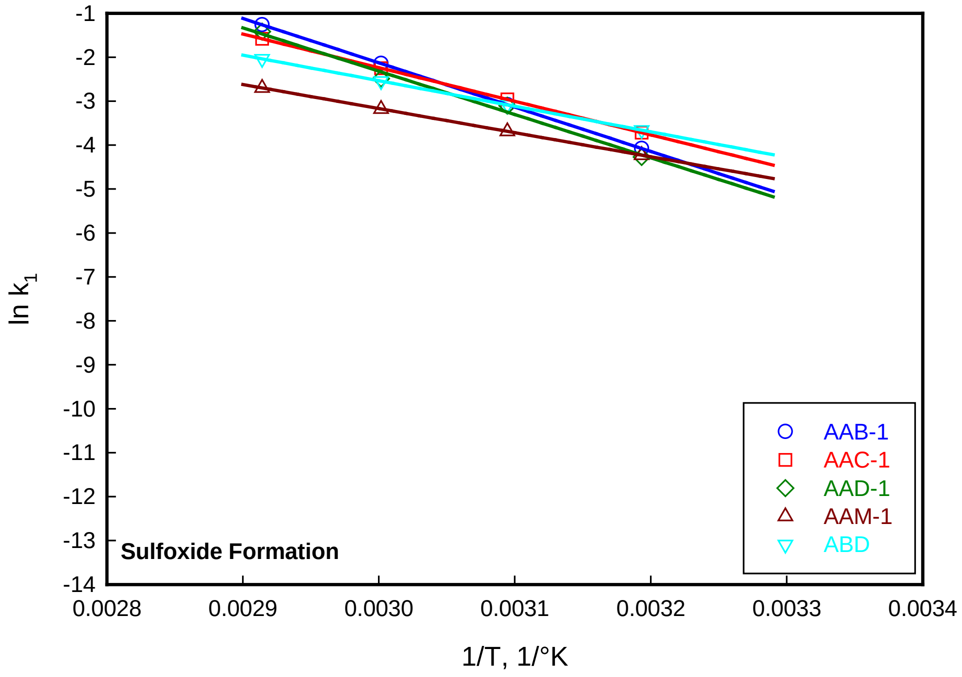

Figure 15. Fast reaction rate coefficient versus reciprocal absolute aging temperature for sulfoxide formation.

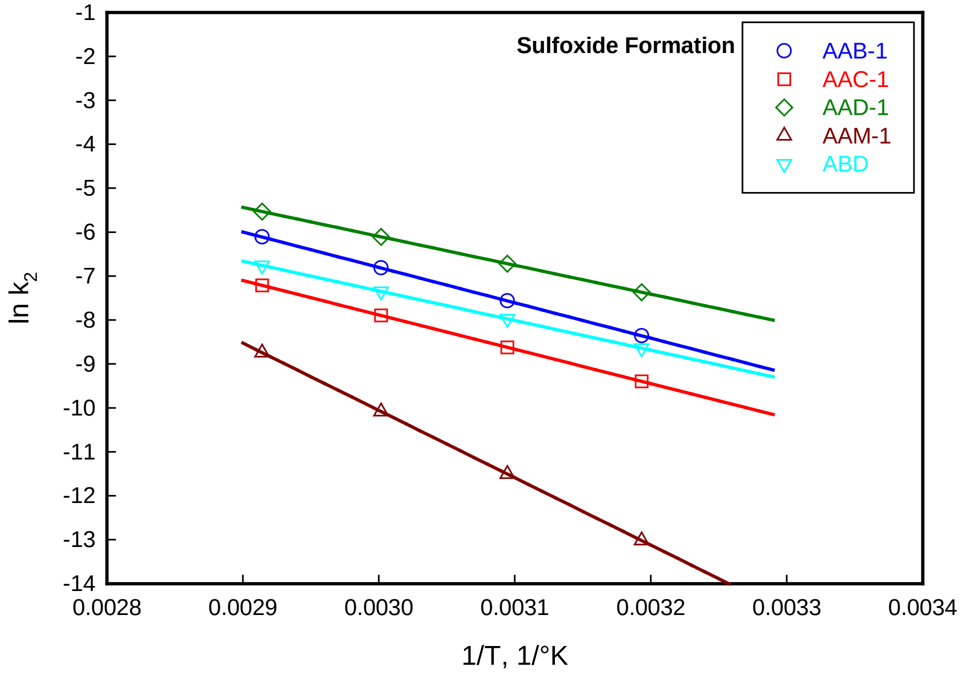

Figure 16.Constant reaction rate coefficient versus reciprocal absolute aging temperature for sulfoxide formation.

The IR spectra for dry and moist aging conditions for different asphalts are shown in Figures 17 through 21. It can be seen that atmospheric aging in the presence of water overlap on top of each other for different asphalts, indicating that laboratory aging at 1 atmopheric pressure in the presence of water does not significantly change the chemical properties of thin asphalt films. Figures 22 through 26 show the presence of water (~3709 cm$^{-1}$) in the samples during moist aging at 60°C. Note that green color presented in the figures is a sample that was prepared intentionally to show water present in an IR spectrum. This sample was injected with 0.5 micro liter of water into the asphalt sample before IR test. It can be seen that aging conducted at ambient pressure does not collect significant amount of water in the samples during aging process. This may explain why small amounts of water present in samples during atmospheric pressure aging do not cause significant change on chemical properties.

How the rheological properties are affected by the small amount of water can be reasonably assumed that rheological properties should not be influenced significantly. This is based on previous research that the change of carbonyl correlated linearly well with the change of rheological stiffness due to oxidative aging.

AAB

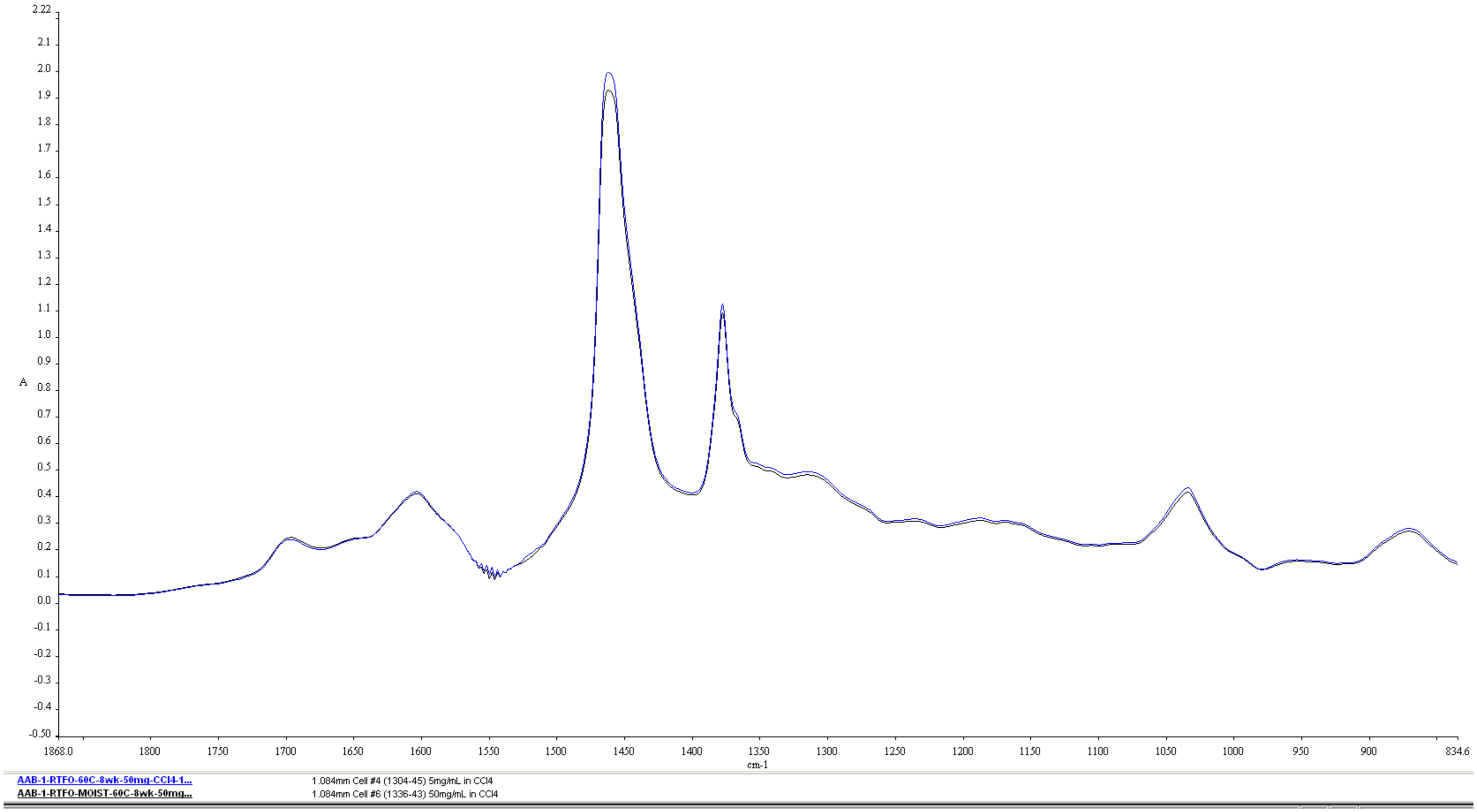

Figure 17. IR spectrum on dry and moist aging for asphalt AAB-1.

AAC

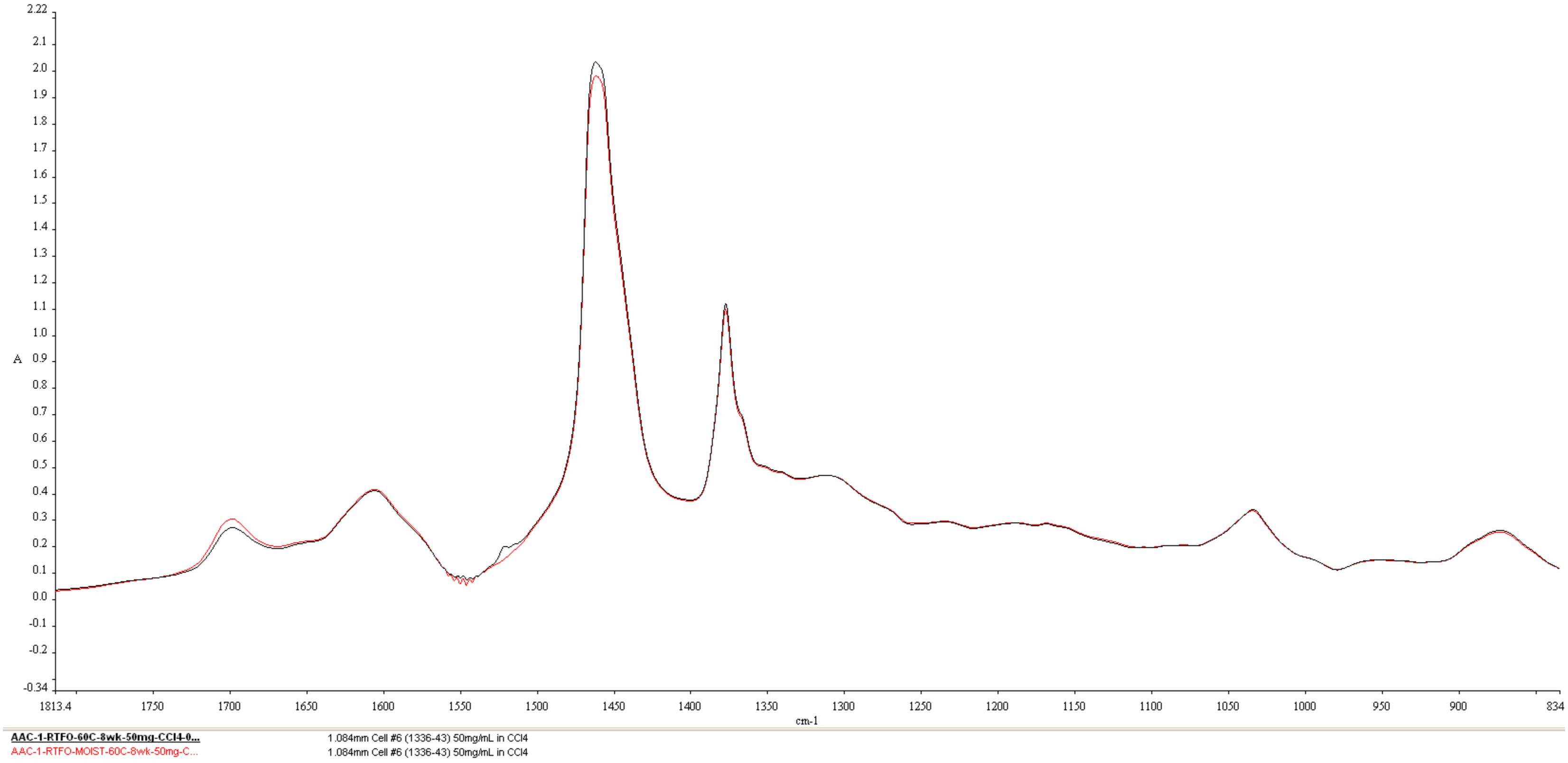

Figure 18. IR spectrum on dry and moist aging for asphalt AAC-1.

AAD

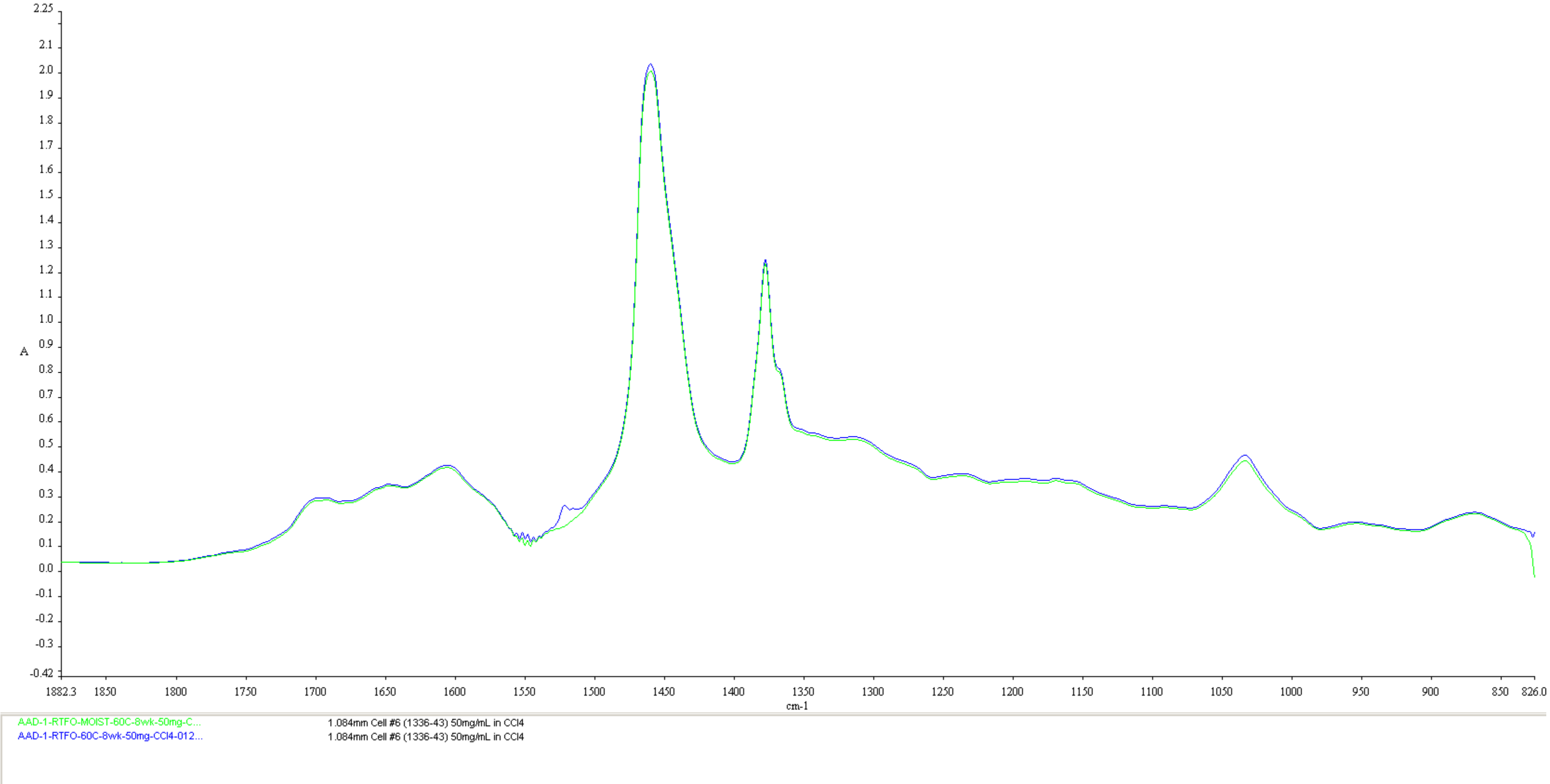

Figure 19. IR spectrum on dry and moist aging for asphalt AAD-1.

AAM

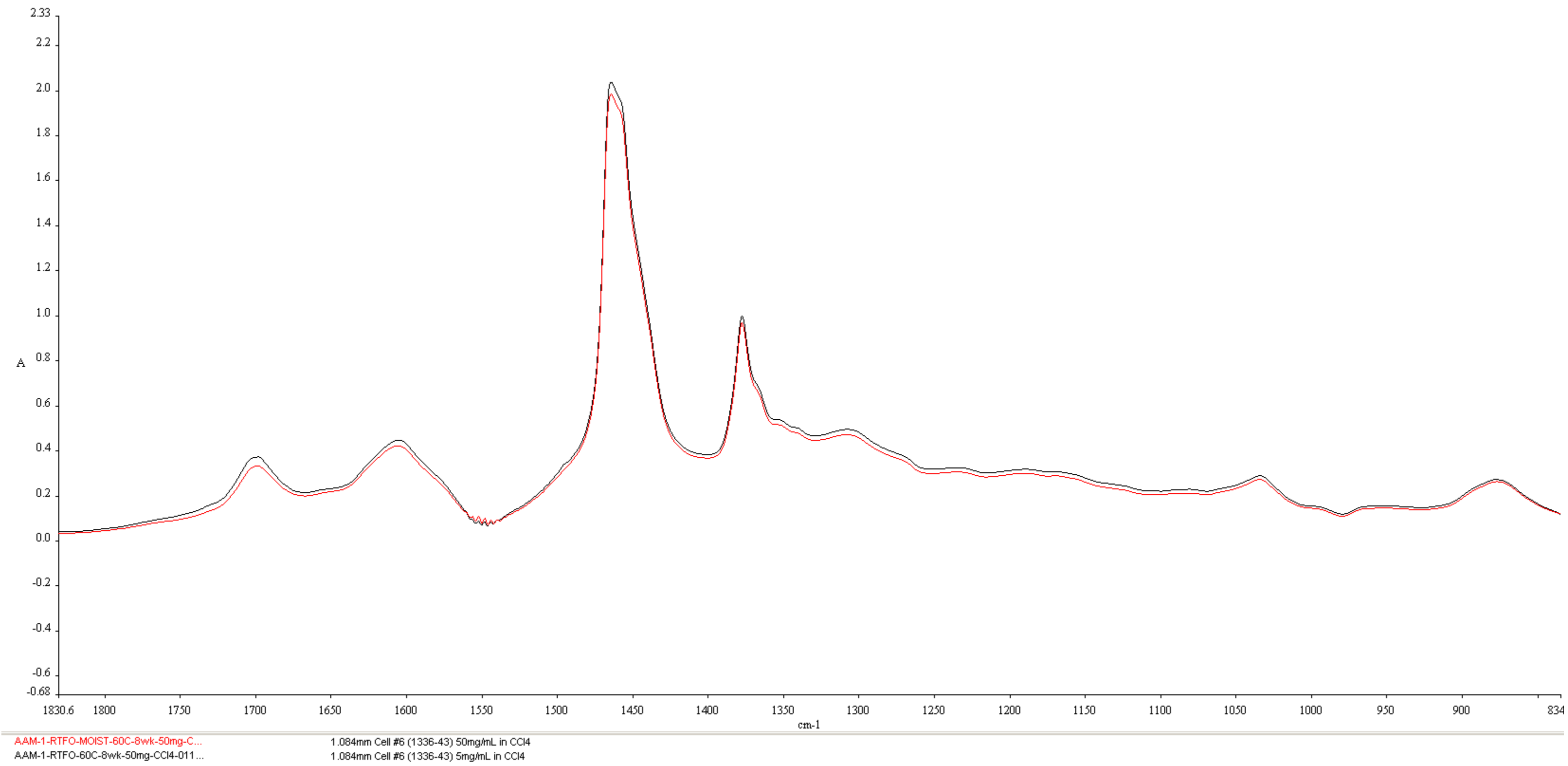

Figure 20. IR spectrum on dry and moist aging for asphalt AAM-1.

ABD

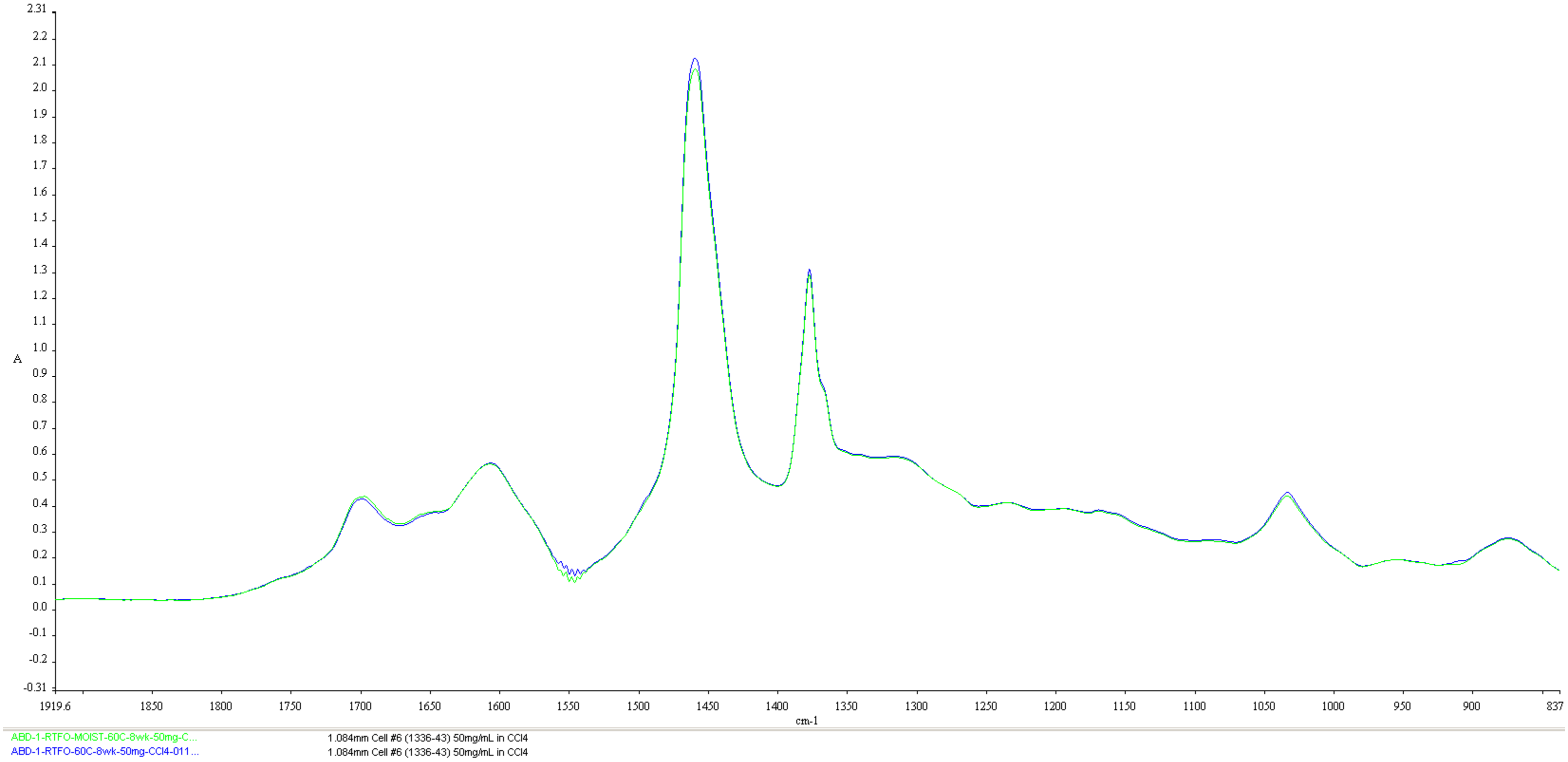

Figure 21. IR spectrum on dry and moist aging for asphalt ABD.

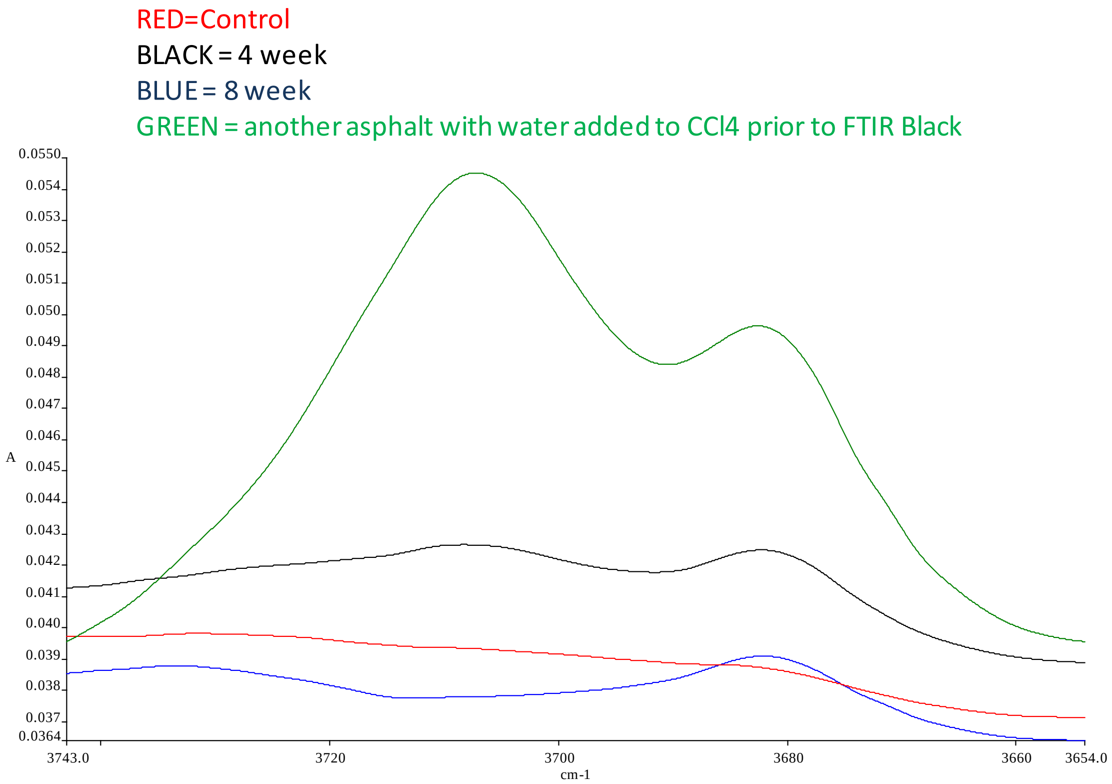

Figure 22. IR spectra for asphalt AAB-1 after 4 and 8 weeks moist aging in terms of water presence.

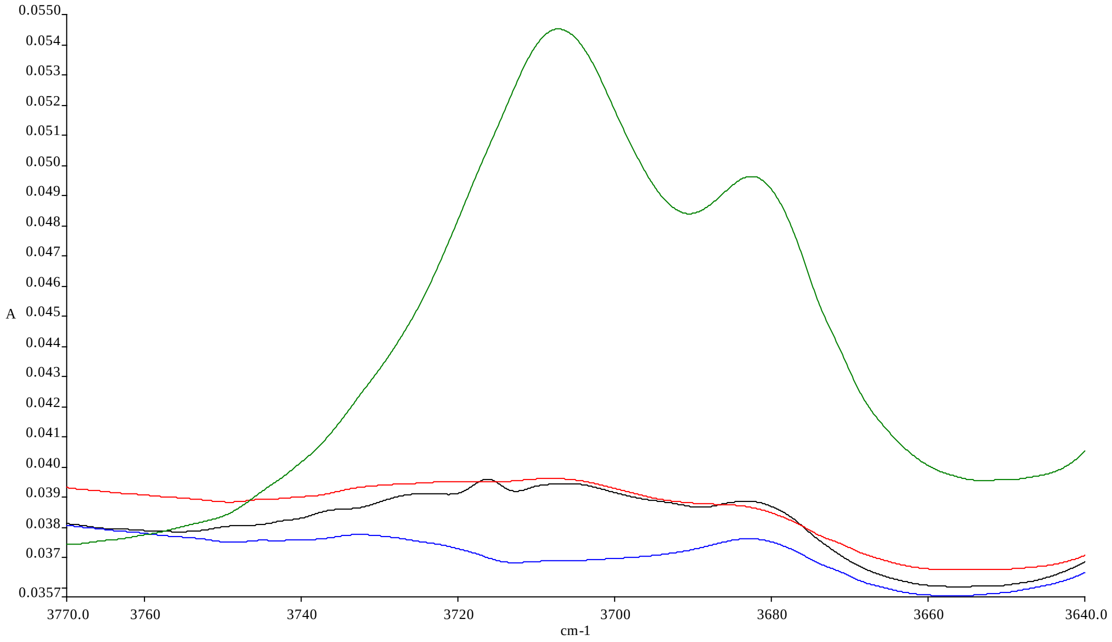

Figure 23. IR spectra for asphalt AAC-1 after 4 and 8 weeks moist aging in terms of water presence.

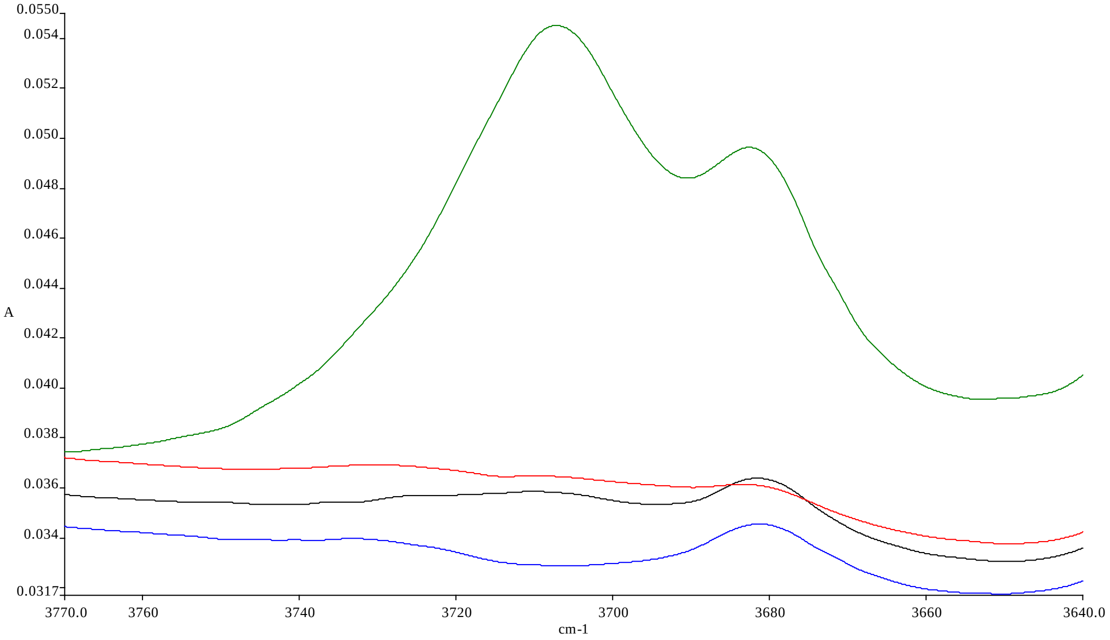

Figure 24. IR spectra for asphalt AAD-1 after 4 and 8 weeks moist aging in terms of water presence.

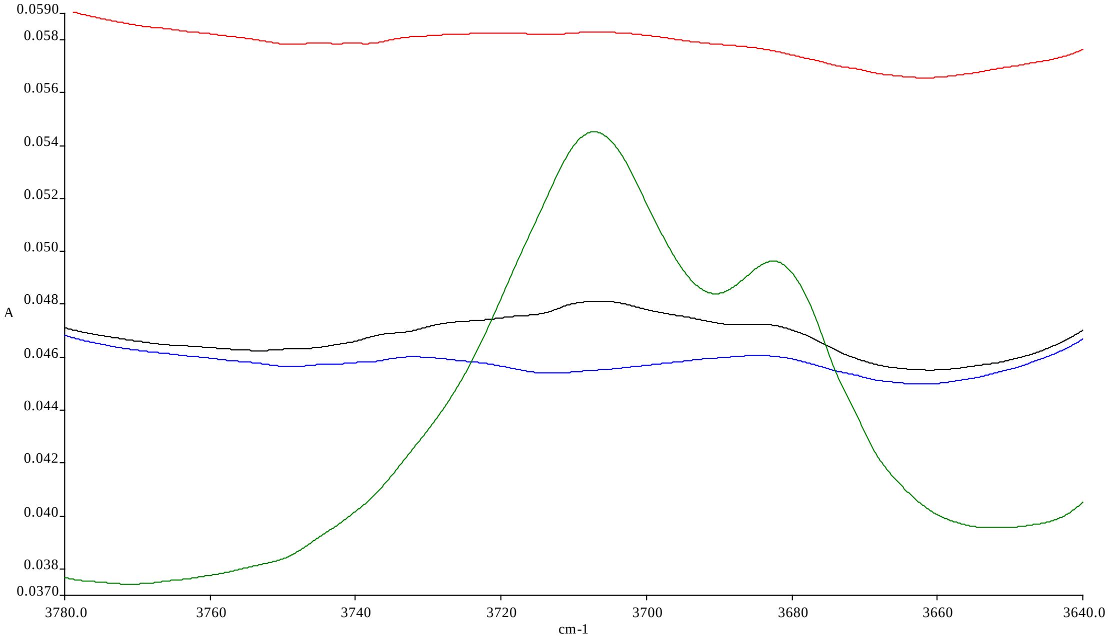

Figure 25. IR spectra for asphalt AAM-1 after 4 and 8 weeks moist aging in terms of water presence.

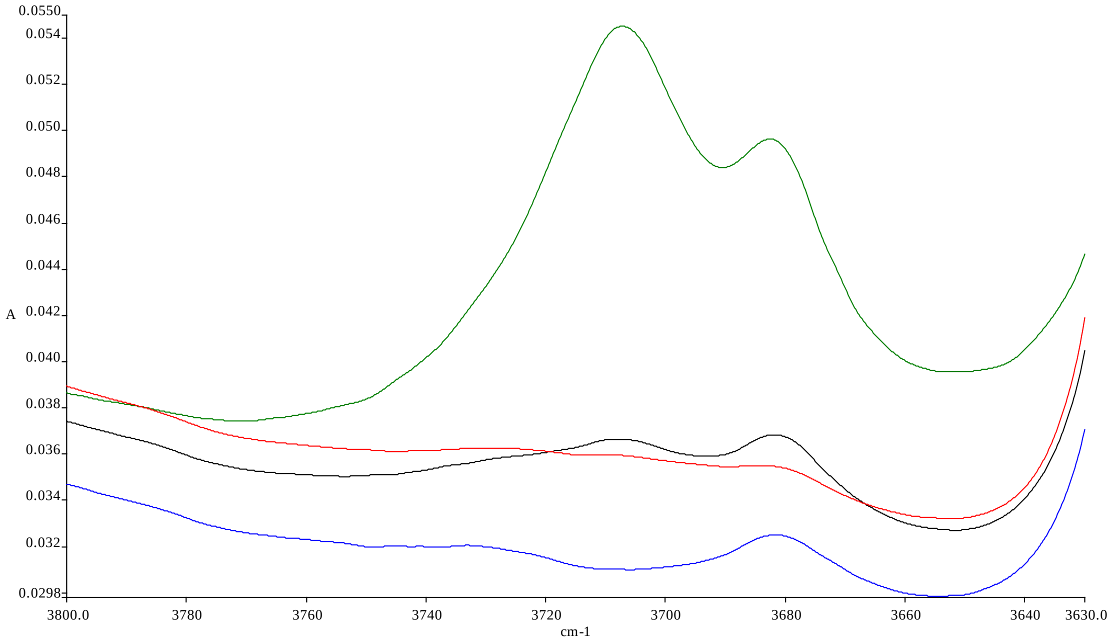

Figure 26. IR spectra for asphalt ABD after 4 and 8 weeks moist aging in terms of water presence.

## Conclusions

The age-hardening characteristics of the asphalt samples were extensively studied by extending the one temperature-time standard points of the convection oven into sets of age-hardening curves representing heat exposure in the field pavement under various temperatures of 40°, 50°, 60°, and 70°C for different durations up to 84 days in the presence of water and absence of water. After the oven exposure, at a given time, each sample was evaluated for its aged chemical properties.

The results indicate that different asphalts show markedly different chemical changes for similar amounts of oxidation. However, convection oven aging in the presence of water does not change the aging process, based on chemical analyses.

From the current results and previous studies, it appears that the impact of water during aging on asphalt stiffness is source dependent and pressure dependent.

It appears that the sensitivity of an asphalt to stiffness increase on oxidation is strongly influenced by its components.

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