Emulsified Asphalt Residue Recovery and Characterization
Combined Use of Moisture Analyzer Balance and Dynamic Shear Rheometer

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A new procedure has been developed for residue recovery of emulsified asphalt. The procedure uses a moisture analyzer balance (MAB). The MAB recovery method is quick and simple compared with traditional recovery procedures such as distillation or oven evaporation. Although the MAB procedure has become an ASTM procedure, there have been a limited number of studies on the rheological properties of the emulsion residues recovered by MAB. This research used a dynamic shear rheometer (DSR) to investigate the rheological properties of MAB specimens. The MAB method was used for several types of emulsions, including cationic and anionic emulsions with several modifications. The MAB method developed in this study addresses the issue of breakdown of polymers during recovery of modified emulsions at high temperatures. The study evaluated the effect of recovery temperature on the recovery time and rheological properties of emulsion residues and proposed a new recovery-characterization procedure. The results show that a preliminary performance grade classification of the emulsified asphalt can be made with the combined MAB-DSR procedure. Furthermore, the study quantified the effect of aging that might occur during the recovery and emulsification process on the rheological properties of the emulsion residues. The combined MAB-DSR procedure is proposed to be a cost-effective alternative method to evaluate the performance of emulsified asphalts.

Background

The United States, which is one of the largest producers of emulsified asphalt, annually produces three million tons of emulsion (1). The increased use of emulsified asphalts has encouraged the asphalt industry to develop standards for characterization and quality control of asphalt emulsion residues. Therefore, it is necessary to recover residues from emulsified asphalts and measure their rheological properties.

In general, more than 10 recovery procedures have been developed. Some of these are oven evaporation, distillation, moisture analyzer balance (MAB), weathering rack, thermostatically controlled hot plate, dehydrator, and the stirred air flow test with nitrogen. These methods have been extensively reviewed in the literature (2). Among these methods, the first three have been more commonly used and have also been incorporated into ASTM and AASHTO standards. The evaporation procedure includes heating 50 g of emulsified asphalt in an open-top beaker at 163°C, for 3 h (3). The distillation method involves heating 200 g of emulsified asphalt in an aluminum-alloy tray at 260°C (4). Some departments of transportation have used 177°C, in place of 260°C, to reduce damage to polymer additives.

Takamura and Lubbers demonstrated that high temperatures (mainly above 180°C) can significantly alter or damage the microstructure of the polymer-modified emulsion and hence the recovered residue will not be representative of the emulsified asphalt recovered in the field (5). Takamura and Lubbers used photomicrographs of emulsion samples taken during 177°C distillation and were able to illustrate that drastic changes in polymer morphology occur even at 177°C. These findings have been further corroborated by King et al. (6). However, the use of moderate temperatures for recovery results in a long recovery time and possibly inaccurate results. For instance, a study conducted by Prapaitrakul et al. (7) demonstrated that the recovered binders from the warm oven (8) method at 60°C might contain small amounts of water.

The MAB method mainly uses a high temperature (up to 163°C) to heat emulsified asphalt (usually 4 g) for a short period of time (typically less than 30 min). MAB recovery is quick, cost effective, and simple compared with traditional recovery procedures such as distillation or oven evaporation. The MAB method is fast because of the larger surface area of the specimens and the use of an advanced infrared-based heating technology. A protocol to use the MAB has been recently incorporated in the form of an ASTM test procedure, ASTM D7404-07 (9). However, there has been little work done to evaluate the properties of the residues from the emulsions obtained.
by MAB. Moreover, the high temperatures that are recommended for use in this method might damage the polymer structure in polymer-modified emulsions. Therefore, it is necessary to investigate the effect of temperature on the speed of recovery and rheological properties of the recovered residue.

Salomon et al. investigated the effects of recovery methods on the rheological properties of the recovered residue (10). They first obtained emulsion residues through the most common recovery methods: MAB, evaporation, and distillation. Then they used a dynamic shear rheometer (DSR) to characterize the emulsion residues. Measuring the complex shear modulus ($G^*$) of the residues at various frequencies and temperatures, Salomon et al. demonstrated that $G^*$ can be used to rank the performance of asphalt emulsions (10). They reported that the measured rheological properties of the residues can vary depending on the recovery method. For instance, Salomon et al. observed the following trend for measured $G^*$:

$$G^*(\text{MAB}) > G^*(\text{evaporative}) > G^*(\text{distillation})$$  \hspace{1cm} (1)

This trend indicated that there might be higher oxidation of the binder during recovery when the MAB method is used. Higher oxidation could be caused by the static nature of the recovery procedure and the higher surface-to-volume ratio of the specimens compared with other methods. In addition, Salomon et al. showed that the MAB method requires a shorter recovery time and less material compared with the other two methods, where the MAB method was at least five times faster (10). These findings have raised a pertinent question about which of these methods can efficiently produce residues that truly represent the cured binders in the field.

This research investigated the efficiency and accuracy of the MAB procedure. The study used a DSR to measure the rheological properties of MAB residues and compare the rheological properties of these residues with the rheological properties of the source binders used to produce the emulsions. Furthermore, to quantify the effect of aging that might occur during recovery, the rheological properties of the source binders were also measured after aging, under the same condition as the emulsified asphalt recovered with MAB. The research also addressed the issues associated with the recovery of modified emulsions at high temperatures. The study proposed a new recovery-characterization procedure by investigating the effect of recovery temperature on the recovery time and rheological properties of emulsion residues. This paper discusses the procedure for emulsion recovery with MAB and measurement of the rheological properties of the recovered binders with DSR.

### MATERIALS

Emulsified asphalts are an oil-in-water type of emulsion with oil droplet sizes that are typically 0.1 to 20 microns in diameter. Asphalt emulsions typically contain 40% to 75% of asphalt binder and 0.1% to 2.5% of emulsifiers and the remainder is water (1). If water is gradually taken away from the system, asphalt returns to its homogeneous, continuous state through flocculation and coalescence (1). Emulsified asphalts, if not stable, can undergo flocculation followed by irreversible demulsification. Long-term or improper storage of emulsified asphalts can also lead to flocculation and coalescence (1).

Asphalt emulsions are typically categorized based on their charge (anionic and cationic) and their rate of breaking (slow, medium, and rapid settings) following ASTM D977 and D2397, selection and use of emulsified asphalt is outlined in ASTM D3628 (11–13). Emulsion nomenclature includes information regarding the type, charge, rate of breaking, viscosity of the emulsion, hardness of the residue binder, and presence of additives. The format that is usually used to name emulsified asphalts contains two to four letters followed by a dash and a number. The two letters right before the dash are indicative of the rate of setting; RS, MS, and SS stand for rapid, medium, and slow setting, respectively. In the case of cationic emulsions, the rate of setting is preceded with the letter C. Sometimes the rate of setting is preceded by HF, which stands for high float. The high float emulsion residues are mainly more resistant to runoff after application. The digit after the dash indicates the viscosity of the emulsion before breaking: 1 for low viscosity and 2 for high viscosity. This is followed by a letter that indicates the type of modification (P for polymer-modified, L for latex-modified, and S for solvent or fuel oil modifier) or the hardness of the asphalt binder residue (H is used for emulsions with harder or stiffer residues).

Each of these types of emulsions has been designed for a specific application. For instance, chip seals require rapid setting emulsified asphalts and cold mixtures require slow setting emulsions. This study included 10 emulsified asphalts intended for a wide range of applications. Table 1 summarizes the materials that were used in the study. To investigate the effect of emulsifiers on the residue recovery and the mechanical properties of the residue, some of the emulsions were produced with the same base binder but different emulsifiers. In all, the 10 emulsified asphalts tested were produced with five base binders. The emulsified asphalts were grouped based on their base binders as shown in Table 1. Samples of the emulsions and the base binders were obtained directly from the producers of the emulsions.

<table>
<thead>
<tr>
<th>Group</th>
<th>Binder Number</th>
<th>Binder’s Name</th>
<th>Group</th>
<th>Binder Number</th>
<th>Binder’s Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B1</td>
<td>CSS-1H</td>
<td>3</td>
<td>B8</td>
<td>CRS-2L</td>
</tr>
<tr>
<td>2</td>
<td>B4</td>
<td>SS-1</td>
<td>4</td>
<td>B9</td>
<td>HFE 100P</td>
</tr>
<tr>
<td>3</td>
<td>B5</td>
<td>RS-2</td>
<td>5</td>
<td>B10</td>
<td>CRS-2P</td>
</tr>
</tbody>
</table>

*AE-90 is a proprietary emulsion that is an anionic, high-float emulsion with medium breaking, used for tack coat.

**HFE 100P is an anionic, high-float emulsion that is polymer-modified.

### TEST METHODS AND RESULTS

This section describes the method used to obtain the emulsion residues and the tests conducted to measure the mechanical properties of the asphalt residues.

#### Residue Recovery

The Sarourious-Mark 3 MAB model was used to obtain residues of the emulsions. The Mark 3 uses an integral monolithic electronic balance with a thermal isolation and an infrared quartz cylinder heating system with controlled airflow to optimize performance.
Approximately 4 g of the emulsified asphalt was poured in a disposable tray and placed inside the closed chamber on the top of the balance. This amount of sample was to ensure that a sufficient amount of residue was obtained for testing with the DSR. Figure 1 shows the MAB device. Salomon et al. used a similar procedure by recovering the emulsion directly in the DSR molds, rather than recovering it in disposable trays and then transferring the residue to the DSR molds for testing (14). The reason for recovering emulsions in disposable trays was to have more surface area and accelerate evaporation.

The termination criterion used to stop heating in the MAB was a weight loss of less than 1 mg in 140 s. This corresponds to approximately less than 0.05% by weight of the remaining residue. Immediately after the moisture analyzer completed testing, the residue was poured in silicon molds for testing with the DSR. This MAB model has a temperature gradient feature and is capable of operating at various temperatures. This feature was used to conduct a preliminary study to investigate the effect of the recovery temperature on the recovery time and the mechanical properties of recovered emulsified asphalts. The preliminary investigation showed that decreasing the temperature from 163°C to 100°C increased the recovery time from an average of 20 min to an average of 90 min.

Although the decrease in temperature significantly increased the recovery time, the increased recovery time was still within an acceptable range compared with other recovery methods. Therefore, it was decided to decrease the recovery temperature for polymer-modified emulsions to 100°C to avoid possible damage to the poly-

![Figure 1: MAB device.](image1)

![Figure 2: Results of MAB tests of emulsions.](image2)
mer chains at high temperatures, as reported by several researchers. Figure 2 summarizes the results from the MAB for the emulsified asphalts. The water content in all the emulsions ranges from 32% to 40%. The residue recovery time for unmodified emulsified asphalts (B1 to B7) was between 10 and 26 min, with an average of 18 min. The recovery time for polymer-modified emulsions was between 57 and 123 min, with an average of 88 min. The unmodified emulsion residues were recovered at 163°C and the polymer-modified emulsion residues (B8 to B10) were recovered at 100°C. The error bars in Figure 2 indicate the repeatability of the MAB test results.

The test results demonstrate that the MAB method has several advantages compared with other methods, such as evaporation and distillation:

- The MAB method is faster because of the larger surface area of the specimens and the use of an infrared-based heating technology. The recovery time for an unmodified emulsified asphalt with the evaporation (3 h) and distillation (1.5 h) methods is typically longer than the average 18 min MAB recovery time (10).
- The advanced heating technology results in uniform heating of the specimens. The isothermal heating and controlled environment yields consistent results, as seen in Figure 2. This finding was further investigated by measuring the rheological properties of the emulsion residues.
- MAB equipment is automated and stops the test as soon as all the moisture is evaporated. This feature means that the residues recovered with the MAB will be more consistent without being subjected to overheating after losing all the water content.
- The high-precision scale used in MAB enhances the accuracy of the measurements.

The consistency of the recovery method was further investigated by measuring the rheological properties of the asphalt residues. The next section will present the test method used to measure the mechanical properties of the asphalt residues. To quantify the effect of aging that might occur during the recovery, the rheological properties of the source binders were also measured after aging under the same condition used to recover the corresponding emulsified asphalt. To produce the aged samples of the source binder, approximately 3 g of the source binder was poured in a disposable tray and placed in the MAB. The temperature and heating duration of the MAB were set to the same temperature and heating duration as was used to recover the residue from the corresponding emulsion. In the remainder of the paper, the binder produced with this aging procedure will be referred to as the MAB aged binder and will be designated by the suffix _Aged.

Rheological Properties

Several research studies have demonstrated that the performance of surface treatments is mainly affected by the mechanical properties of asphalt binder residue. Therefore, it is necessary to measure the mechanical properties of asphalt residue for the purposes of material selection and quality control. There are many test methods that can be used to characterize asphalt emulsion residues. These methods include conventional tests (such as penetration, ductility and ring and ball) and performance-based tests (such as DSR and bending beam rheometer).

In this study, to measure the materials’ rheological properties over a wide range of loading conditions, the DSR (Model TAAR2000Ex) was used. The typical test geometry to use with a DSR is a cylindrical specimen between two parallel plates with the top plate being subjected to torsion and the bottom plate being fixed, as in Figure 3. The specimens had diameter 25 mm and height 1 mm.

Within the parallel plate test geometry, the shear strain rate at any point depends on the distance from the axis of rotation; therefore, the material will be subjected to different strain rates and stress levels at different radial positions within the specimen. As a result, in the case of a material that exhibits a nonlinear response, the measured response with the parallel plate geometry is an average of the nonuniform response across the cross section of the specimen (15).

The DSR was used to measure the mechanical properties of the binder residues, source binder, and MAB aged binder. To obtain the mechanical properties of these materials under varied loading conditions, a combination of frequency and temperature sweep tests were conducted. The material response under sinusoidal oscillatory loading (at varied frequencies and temperatures) was measured with the DSR. The oscillatory tests were conducted at five temperatures where the frequency was changed linearly from 25 to 1 Hz, in intervals of 1 Hz. The test temperatures were 30°C, 45°C, 58°C, 64°C, and 70°C. All the tests were conducted at low stress levels to avoid any nonlinear behavior or instability flow (15, 16).

Figure 4 illustrates the measured dynamic shear modulus of asphalt binder B3 (SS-1H) as a function of frequency and temperature. The results measured with the DSR are consistent across the
replicates. Similar results were observed for other emulsions tested in this study. Statistical analyses were conducted for further investigation of the variation in the DSR-measured mechanical properties of the MAB recovered residues. As an illustration, Figures 5 and 6 present the DSR test results for four loading conditions: loading frequencies of 5 and 15 Hz and test temperatures of 30°C and 58°C. The error bars in Figures 5 and 6 reflect the combined variability caused by differences in the residue samples recovered with the MAB as well as differences in the DSR measurement. The results further corroborate the consistency of the MAB in recovery of asphalt emulsions.

To examine the combined effect of the emulsification process and aging during recovery on the mechanical properties of the asphalt binder residue, the mechanical properties of the base binders were measured and used to produce the tested emulsions. To differentiate the changes caused by the emulsification process from the changes caused by aging during recovery, the mechanical properties of the MAB aged binders were measured. Figures 5 and 6 also compare the mechanical properties of the base binder with its corresponding MAB aged binder. The results indicate that aging caused by MAB recovery is not significant. With the exception of Group 1, which has a high standard deviation, the change in dynamic shear modulus caused by aging is less than 7%. The results also demonstrate that in most cases the residues have similar or higher (albeit insignificantly higher) modulus compared with their corresponding MAB aged binder.

The data can be used to distinguish between the effect of aging during recovery and emulsification on the mechanical properties of the binder residue. For instance, the moduli of recovered binders in Group 2, especially AE-90, are significantly higher than the aged base binder. AE-90 is an HF emulsion and the gel property of HF emulsions alters their rheology compared with the base binder. This increase in modulus could also be caused by the emulsion production process, chemical reaction, higher aging in the emulsions, or any combination of these factors. Furthermore, the results illustrate that decreasing the recovery temperature for polymer-modified emulsions (Groups 3 to 5) to 100°C reduces the risk of damaging the polymer chains, as was reported for recoveries at a high temperature of 163°C.

![Graph showing measured dynamic shear modulus at 30°C](image)

**FIGURE 5** Measured dynamic shear modulus at 30°C: (a) 5 Hz frequency and (b) 15 Hz frequency (Base = source binder used to produce emulsion; Base_Aged = source binder aged with MAB and same procedure as emulsion).
Another pertinent observation from these results is that the modulus of recovered asphalt from the emulsion CMS-2 is drastically less than the base binder. This is most likely because the CMS-2 emulsion utilizes a solvent, such as naphtha or kerosene, to improve the workability and even a small amount of the solvent left in the residue after recovery will significantly reduce the modulus. In general, it is not recommended to use the MAB procedure for recovery of fuel-based emulsified asphalts. ASTM D7404 provides specific guidance for use of the MAB procedure for these types of emulsified asphalts (9). However, CMS-2 was included in this study to illustrate the issue with recovery of solvent-based emulsified asphalts with MAB.

To conduct a more comprehensive comparison of the base binder, MAB aged sample, and binder residue; the results from the frequency-temperature sweep tests were used to construct and compare master curves. The Christensen–Anderson–Marasteanu model was used to construct master curves (17):

\[ |G^*(\omega)| = G_s \left[ 1 + \left( \frac{\omega}{\omega_c} \right)^n \right]^{\nu - \nu_w} \]  

where

\[ |G^*(\omega)| = \text{absolute value of complex modulus as function of frequency, } \omega; \]

\[ G_s = \text{glassy modulus and log } |G_s| \text{ is considered to be fixed at 9.1; and} \]

\[ \omega_c, \nu, \text{ and } w = \text{model parameters.} \]

Figures 7 and 8 illustrate the master curves for each base binder, its MAB aged sample, and the residues from its corresponding emulsions. Considering master curves for the base binders as a reference, these graphs depict the effect of aging and emulsification on the mechanical properties of MAB aged binder and the recovered residue. The gray area in the figures indicates 10% deviation from the modulus values for the base binder. The figures demonstrate that aging caused by the MAB recovery is not significant and the change in modulus is typically less than 7%.

The master curves also illustrate that emulsification results in binder residues with higher stiffness, even when compared with the MAB aged base binder, at lower frequencies. These differences are
not substantial for the emulsified asphalt binders in Groups 1, 4, and 5. However, the differences are more significant for the emulsified asphalts in Group 2, especially AE-90. The significant change in the modulus of AE-90 could be caused by the recovery of this HF emulsion at high temperature and needs to be further investigated.

In general, the difference between the modulus of residues and the MAB aged binders could be caused by the emulsification process, additional aging of the asphalt binder particles during recovery with MAB, the chemical reaction between the emulsifier and the asphalt binder, or a combination of these factors. In addition to AE-90, another exception was that the modulus of CRS-2L residue (in Group 3) was also significantly higher than the MAB aged binder, especially at low frequencies. In this case, the change in modulus was expected because the modifier was injected into the system during the production of the emulsion, rather than modifying the base binder first and then producing the emulsified binder from the modified binder. The latter was the process used for producing modified emulsified binders in Groups 4 and 5.

Finally, to quantify the effect of aging and emulsification on the performance of the residues, the study also measured the high-temperature performance grade (PG) of the tested materials: base binders, MAB aged binders, and emulsified asphalt residues. The unaged criterion of $G'/\sin\delta=1.0$ kPa, where $\delta$ is the phase angle, was used to determine the high-temperature grade for all binders. Table 2 summarizes the high-temperature PG of these materials and the change in the high-temperature grade caused by aging and the emulsification process. The increase in the high-temperature PG is typically less than 4°C. However, in the case of HF emulsified asphalts (AE-90 and HFE 100P), the increase in high-temperature PG can reach up to 10°C.
FIGURE 8  Master curves at 58°C for emulsified asphalts: (a) Group 3, (b) Group 4, and (c) Group 5 (MAB recovery and aging conducted at 100°C).
### SUMMARY AND CONCLUSIONS

Use of the MAB is already documented as an ASTM procedure for recovering emulsified asphalt residue (9). This recovery method is quick and simple compared with traditional recovery procedures such as distillation and oven evaporation. However, several research studies have reported that the high recovery temperature of 163°C, recommended for use with the MAB, might damage the polymer chains in the polymer-modified emulsions and cause a decrease in the stiffness of the residues. This study used DSR to investigate the efficiency of the MAB procedure based on its recovery time as well as its ability to produce residues that are representative of the field. The study also quantified the effect of aging associated with this recovery method. The following is a summary of some of the findings from the study:

- Investigating the effect of temperature on recovery time and the mechanical properties of the emulsion residues, the results showed that the recovery temperature for modified asphalt binders can be decreased to 100°C to avoid the risk of damaging the polymer in the binder. This was verified by comparing the rheological properties of emulsion residue with the properties of the base binder used to produce these emulsions.
- The results demonstrated that aging during recovery with MAB is not significant and the change in modulus of MAB aged binders is less than 7% compared with their respective original binders.
- The results showed that some of the emulsion residues have a higher modulus at lower frequencies or high temperatures, even when compared with the MAB aged base binder. This increase in modulus could be caused by the emulsion production process (e.g., use of acids and bases), greater aging of asphalt binder particles in emulsified asphalt during recovery with MAB, a chemical reaction between the emulsifier and the asphalt binder, or any combination of these factors.

This paper presented a procedure for emulsion recovery with MAB and measuring the mechanical properties of recovered binders with DSR. It was demonstrated that a preliminary, high-temperature PG classification of the emulsified asphalt can be made with the combined MAB-DSR procedure. The results also demonstrated that the MAB-DSR procedure is not only fast, but it is reliable and consistent, based on the MAB and DSR results. The study proposed the combined MAB-DSR procedure as a cost-effective alternative method to assess the performance of emulsified asphalt residues at high and intermediate temperatures. This method can be used (a) for quality control and developing specifications for emulsified asphalts and (b) for predicting the performance of treatments that use asphalt emulsions.

### REFERENCES


