

## **EFFECT OF RECOVERY METHOD ON THE PROPERTIES OF CQS EMULSION RESIDUES AND THEIR CORRELATION TO MICRO SURFACING PERFORMANCE**

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### **ABSTRACT**

Atmospheric or vacuum distillation techniques are traditionally used for residue recovery of bitumen emulsions. This is less than ideal for emulsions containing polymers, especially elastomeric polymer lattices, due to the inability to capture the full performance of the polymer modified residue that takes place in the real-life application. This happens as a result of thermal degradation of the polymers due to exposure to high temperatures, or because of the inability to capture the true polymer network morphology due to kinetic limitations. As a result, evaporative techniques of residue recovery for bitumen emulsions were developed and standardized.

The current paper is taking a more in-depth look at the effects of residue recovery on Micro Surfacing emulsions and its impact on measuring and predicting field performance. A number of cationic quick setting emulsions for micro-surfacing with SBR polymer contents between 0 and 6% were produced in the lab under carefully controlled conditions. Residue recovery was performed using the classical distillation technique and the newly developed low temperature evaporative technique described in ASTM D7497-09. A number of rheological tests such as complex modulus determination, multiple stress creep recovery, dynamic master curves, etc. were performed on emulsion residues collected from both methods, to quantify the effect of the polymer dosage on the viscoelastic properties of the emulsion residues. The same emulsions were then used preparing carefully controlled Micro Surfacing specimens. The cured samples were tested for wet track abrasion loss and the vertical and lateral displacement under a loaded wheel. Correlations between properties of the emulsion residues from both recovery methods and performance of the micro-surfacing formulations were determined.

### **1.0 INTRODUCTION**

Residue recovery of polymer modified bitumen (PMB) emulsions has been one of the main focuses of research during the last few years. With PMB emulsions gaining market share, it became evident that classical distillation procedures, even adjusted for temperature, were not capturing the true or full contribution of the polymer component within the bituminous residue. The need for alternative recovery procedures became a priority for the researchers involved in the ever growing area of bitumen emulsions.

With residue recovery being one step as part of bitumen emulsion specifications, the potential replacement of distillation as we know it with other methods of residue recovery has opened the need to revise or re-adjust entire testing protocols and specifications. Several new methodologies for retrieving the residue were developed or are now in experimental stages [1]. Some of these include a newly standardized evaporation recovery method, residue recovery by moisture balance analyzer, Karl Fischer titration, etc. All these newly developed or adapted methods will deviate from traditional distillation either by process duration or by the quantity of bituminous residue it generates. This will affect bitumen emulsion testing specifications as we know them.

### **2.0 SCOPE OF WORK**

Residue recovery by evaporation is a newly developed method to replace the distillation. It was recently adopted and standardized under ASTM D7497 [2]. As part of the drive to more accurately capture the contribution of the polymer fraction in PMB emulsion residues, the evaporation recovery method allows 48 hours for the entire process, as opposed to 1-1.5 hours. The rationale behind the evaporation method is that exposing elastomers to 205°C, even for a short time, is not something that occurs in real life in any processes on the road where PMB emulsions are utilized. High

temperature can lead to partial thermal degradation in SBR type polymers.

Polymer contribution on performance is not only a function of content but also a function of morphology. Specific polymer structures develop in real life processes within the bituminous binder, i.e. honeycomb-type structures in case of curing emulsions containing SBR lattices [3]. One important factor in the development of specific polymer morphologies is kinetic. In other words, even a vacuum distillation of PMB emulsions, exposing the material to much lower temperatures, will still fail to re-create specific polymer morphologies due to the short duration of the residue recovery process. Time is needed for these steric structures to form.

The ASTM D7497 evaporation recovery process is using a thin film of bitumen emulsion which cures at room temperature for the first 24 hours, followed by another 24 hours at 60°C in a forced draft oven. There is limited data available to describe how the evaporation process will affect PMB residue properties compared to the ones obtained by the classic established distillation protocol. It is one of the purposes of the current study to compare the physical and rheological properties of the residues, obtained by both the distillation and the evaporation methods, of a series of emulsions designed and produced with carefully controlled compositions.

Furthermore, our intention was to take this study beyond strictly testing the recovered materials. The type of emulsions selected belongs to the Micro Surfacing emulsion type, cationic emulsions with fairly complex and precise emulsifier chemistries. They also contain polymer, usually of an elastomeric type. The emulsion chemistry together with the polymer type, content and morphology translates into a set of properties within the Micro Surfacing application. It was our intention to try to determine how big is the contribution the binder modification brings to Micro Surfacing performance and how well is it captured by the distillation and the evaporation residue recovery procedures.

### **3.0 EXPERIMENTAL WORK**

#### **3.1 Materials and Specimen Preparation**

The emulsions used for the current project were all lab prepared sample of the CQS-1HP type. The asphalt cement used for the preparation was an 80/100 penetration grade and the crude it originates is of Western Canadian origin. For the preparation of the lab emulsion samples, the emulsifier used was a commercial emulsifier available for micro surfacing emulsions and the polymer used was commercially available SBR latex containing sulphur as a crosslinking agent.

The PMB Micro Surfacing emulsion series consists of 7 emulsions of similar formulations (same bitumen type and grade, same emulsifier type and dosage, same target residue, same manufacturing parameters and equipment). The only variable is the SBR content, which varies from 0 to 6% in increments of 1%. All 7 samples were produced in the McAsphalt lab using a Raschig lab emulsion mill. In our current study the emulsions will be labelled "0" to "6" for simplicity purpose, the number corresponding with the SBR polymer content.

Subsequently, each of the emulsions was used for preparing specimens for testing the Wet Track Abrasion Test (WTA) [4] and the Loaded Wheel Test (LWT)[5], both standard tests utilised as part of designing Micro Surfacing applications under the current ISSA guidelines. Duplicate specimens were prepared for each emulsion type and for each test. For the Micro Surfacing application, the selected job mix formula belongs to an established design used extensively by McAsphalt in Ontario. The aggregate used is a meta-gabbro (basaltic) type aggregate of very high quality and the gradation fits an ISSA Type III band. The Micro Surfacing formulation used for designing the WTA and LWT specimens contains 12.0% CQS emulsion and 1.0% Portland cement additive to the total aggregate.

#### **3.2 Testing Protocols**

Once the emulsion preparation was complete, each sample was tested using the distillation protocol (ASTM D6997)[6] and the evaporation protocol (ASTM D7497) [2]. The maximum distillation temperature was 260°C for the emulsion containing no SBR polymer and 205°C for all other emulsions containing polymer. After the residue was recovered, each sample was loaded into a Dynamic Shear Rheometer. Full rheological test were completed on both the evaporation and the distillation residues. Dynamic data was collected over temperatures covering the viscoelastic domain of the binder and Black Curves were generated over the same temperature range. Multiple Creep Stress and Recovery (MSCR, ASTM D7405) [7] data was collected at 64°C, also  $G^*/\sin(\delta)$  at 64°C was

measured. In addition, classic bituminous residue tests were done on the specimens, such as Penetration at 25°C (ASTM D5)[8] and Softening Point by Ring and Ball [9]. For reasons of ensuring that the emulsions are as close as possible in properties, other than the SBR polymer content, particle size analysis was done on all samples, using a Horiba laser scattering particle size analyzer. The WTA Micro Surfacing specimens were prepared and cured, then soaked for 6 days in a water bath at room temperature. LWT and WTA specimens were tested as per the ISSA protocols [4][5].

#### 4.0 EXPERIMENTAL RESULTS

The testing results for the emulsions "0" to "6" and the penetration and softening point results on the distillation residues are presented in Table 1.

**Table 1. Test Results on CQS Emulsions "0" to "6"**

% SBR Latex	"0"	"1"	"2"	"3"	"4"	"5"	"6"
Residue by Distillation, %	64.9	65.5	65.9	64.6	65.0	67.5	66.6
Pen on Distillation, dmm	76	71	71	62	60	54	50
Softening Point on Dist, °C	46.5	51.0	53.5	61.0	62.0	-	-
Median Particle Size, microns	3.886	3.552	3.533	3.319	3.488	3.300	3.104
Residue by Evaporation, 48h, %	66.6	66.0	66.1	65.1	67.1	68.2	67.7

The DSR test results at 64°C and the MSCR on-recoverable creep compliance and Recovery (at 3200 Pa), tested at 64°C for both the distillation and the evaporation residues are shown in table 2.

**Table 2. Rheological Parameters of CQS Emulsions "0" to "6"**

% SBR Latex	"0"	"1"	"2"	"3"	"4"	"5"	"6"
Jnr Distillation, 64°C, kPa	10.757	4.752	3.307	1.459	0.857	0.700	0.374
Jnr Evaporation, 64°C, kPa	5.620	4.309	3.200	1.919	1.383	0.925	0.673

Recovery Distillation, 64°C, %	0	20.7	30.5	46.9	52.1	56.6	63.2
Recovery Evaporation, 64°C, %	0.4	2.7	7.6	16.7	23.4	30.0	37.7
G*/sin( $\delta$ ) Distillation, 64°C, kPa	0.9	1.6	1.97	3.02	3.79	4.14	5.87
G*/sin( $\delta$ ) Evaporation, 64°C, kPa	1.85	2.07	2.81	4.02	5.05	5.86	7.07

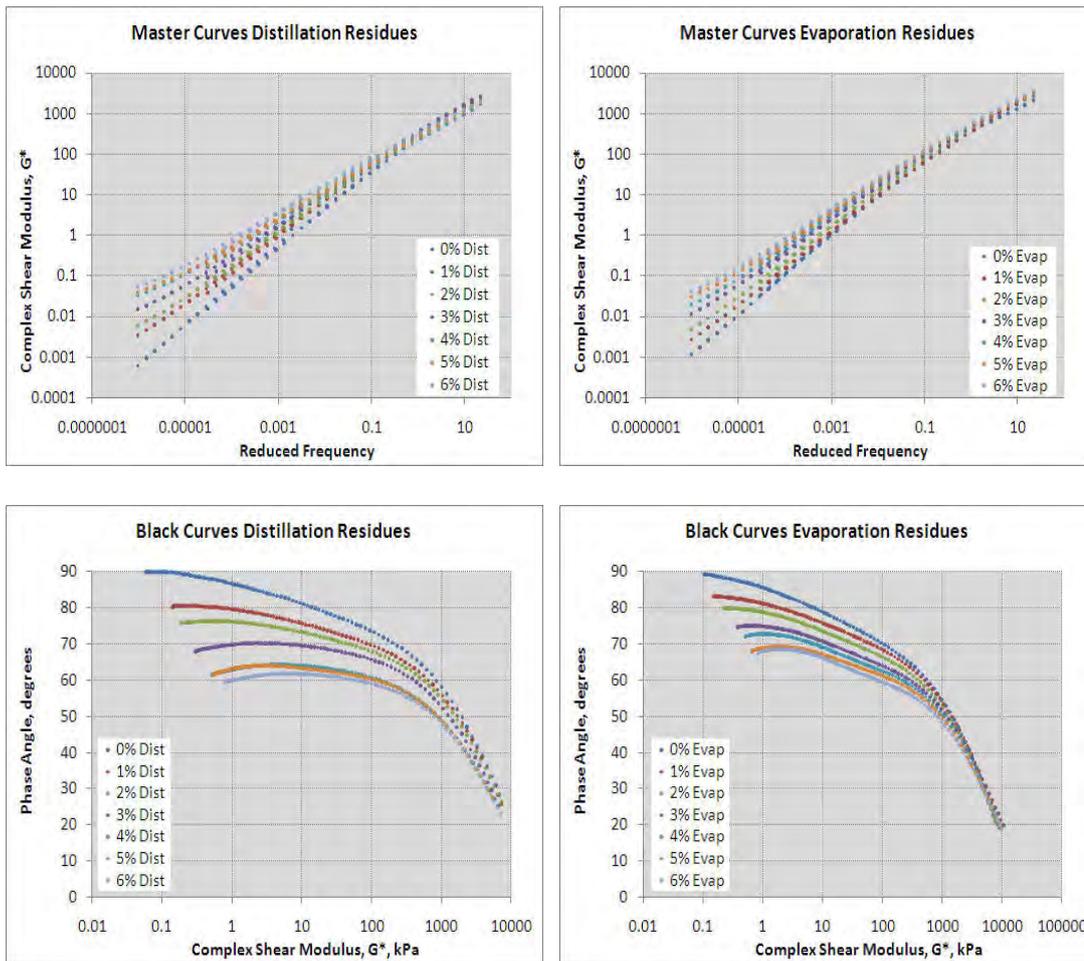
The collected dynamic data on the residues was converted into master curves. The shifting was done to a reference temperature of 20°C using the WLF formula and the shift factor coefficients used were 11.6 for C1 and 90 for C2. The master curves for the distillation and the evaporation residues are presented in Figures 1 and 2. The evidence of polymer becomes more visible at lower reduced frequencies, as expected. Black curves for the same evaporation and distillation residues are shown in Figures 3 and 4.

Results of the 6 days soaked WTA tests as well as the vertical and lateral displacements measured using the LWT are summed-up in table 3.

**Table 3. WTA and LWT Results for CQS Emulsions "0" to "6"**

% SBR Latex	"0"	"1"	"2"	"3"	"4"	"5"	"6"
WTA Loss, g/m <sup>2</sup>	136.7	123.5	116.9	115.3	113.6	107.0	92.2
LWT Lateral Displacement, %	5.77	9.39	3.07	4.21	4.18	6.24	6.63
LWT Vertical Displacement, %	39.70	55.39	33.38	30.35	33.71	37.74	38.93

**Fig 1-4 Dynamic Master Curves and Black Curves for CQS "0" to "6" Residues**



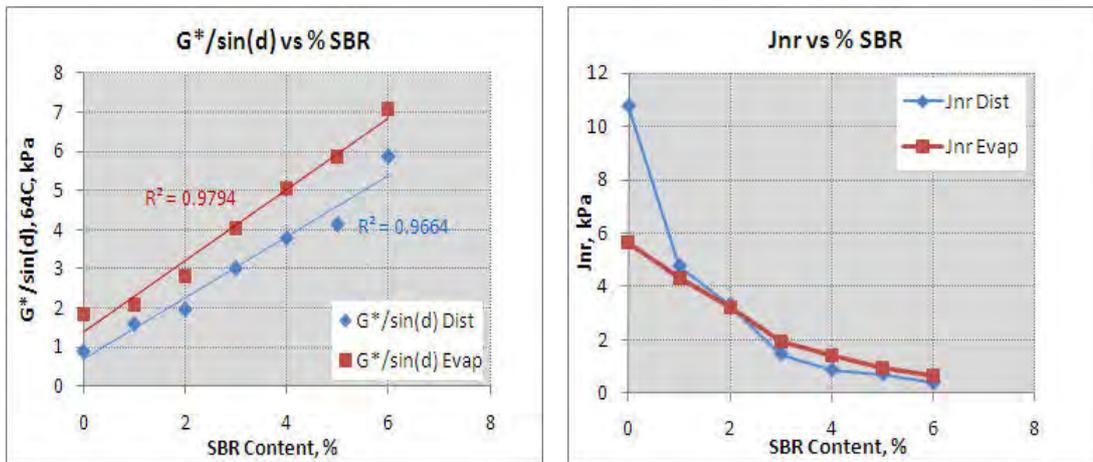
## 5.0 DISCUSSION OF THE RESULTS

If we analyze the residue data obtained by the two recovery methods described, a few observations arise. It was mentioned in literature before [10] that there is evidence that the evaporation recovery method ages the bitumen more than the distillation. This observation is supported here first by the higher  $G^*/\sin(\delta)$  values seen for the evaporation residues. The 85/100 bitumen used for preparing the emulsions has a  $G^*/\sin(\delta)$  at 64°C very close to the 0.9 kPa obtained after distilling the 0 emulsion. The "0" evaporation residue  $G^*/\sin(\delta)$  at 64°C is essentially double, meaning the evaporation recovery procedure induces roughly the same degree of aging as an RTFO aging procedure on a virgin PG bitumen.  $G^*/\sin(\delta)$  at 64°C for distillation and evaporation residues are plotted in Figure 5.

The same aging is evident in the  $J_{nr}$  values for the "0" emulsion residues, the  $J_{nr}$  "0" evaporation shows a binder about twice as stiff as the "0" distillation. However, while the  $G^*/\sin(\delta)$  at 64°C evaporation values maintain the higher values for all 7 evaporation residues, the same is not valid for the  $J_{nr}$  results, shown in Figure 6. With the increase in polymer content, the  $J_{nr}$  values became very close, the distillation residues actually showing lower compliance values than the evaporation. One possible explanation for this behaviour is that the SBR latex containing sulphur leads to a partial crosslinking of the polymer when exposed to the high temperatures of the distillation process. While the  $G^*/\sin(\delta)$  is unable to show this, the MSCR test is much better suited to capture the existence and the robustness of a polymer network, hence the lower  $J_{nr}$  and higher Recovery results for the distillation residues.

**Fig 5.  $G^*/\sin(\delta)$  vs. % SBR SBR**

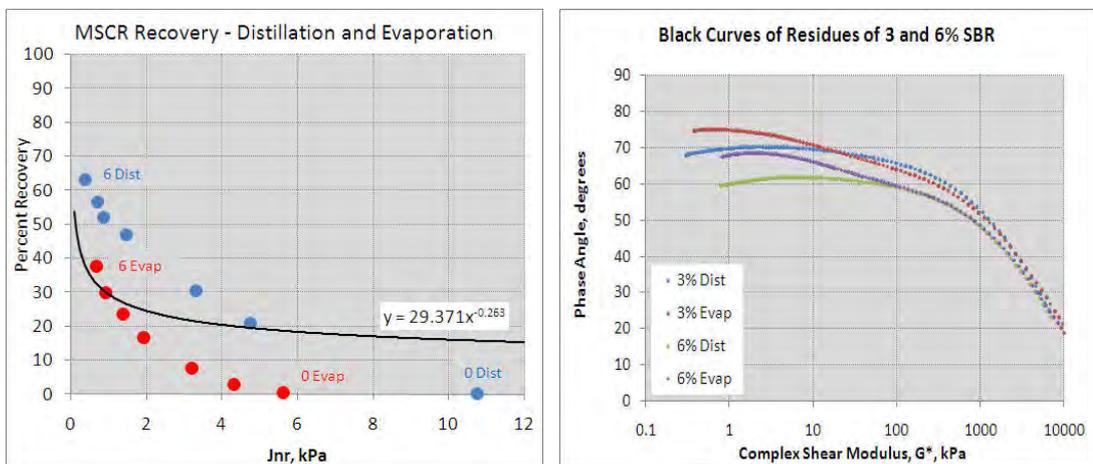
**Fig 6. Non-recoverable Creep Compl. vs. %**



This makes an interesting case when the elastic behaviour of a residue is measured using the newly developed MSCR criteria, where a binder is considered elastic if  $R > 29.371 \times J_{nr}^{-0.263}$ . By plotting the MSCR results of both residue series (Fig. 7), it becomes evident that according to the afore mentioned criteria, a distillation residue of the 1% emulsion is already considered elastic, while the first evaporation residue to barely pass the elasticity criteria is the 5% SBR. The very different elastic behaviour of the evaporation vs distillation residues is also visible when analyzing the plotted Black curves. Figure 8 shows a graph containing the Black curves of the residues of the 3% SBR and the 6% SBR emulsions. Noticeably lower phase angles for the distillation residues are evident for complex shear moduli values of below about 50 kPa or so.

Fig 7. MSCR Elastic Behaviour of Residues

Fig 8. Black Curves for 3 and 6% SBR



Given that both residue series originate from the same emulsion samples, it is evident that the two residue recovery methods produce bitumens having very different properties. The evaporation recovery is aging the bitumen phase more but seems to develop a weaker polymer network, at least when using SBR lattices containing crosslinking agents. It will be interesting to see if SBR lattices having no crosslinking agents exhibit the same behaviour. Also, the question remains which of the two recovery procedures reproduces more accurately the behaviour of the binder in paving applications in the lab and the field.

Fig 9. WTA Loss vs % SBR

Fig 10.  $J_{nr}$  vs WTA Loss

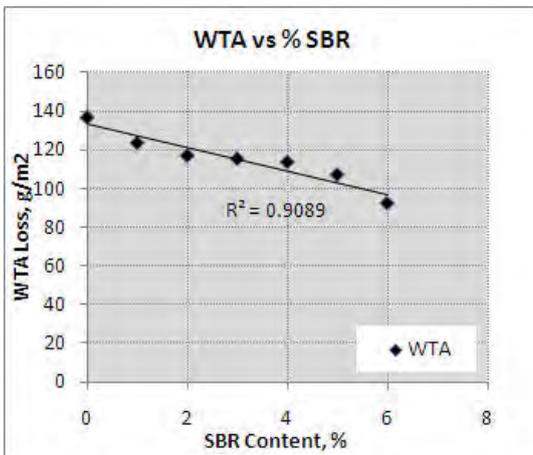


Fig 11. MSCR Recovery vs WTA Loss

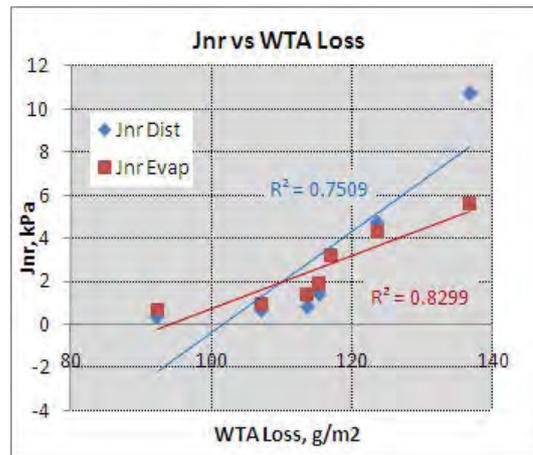
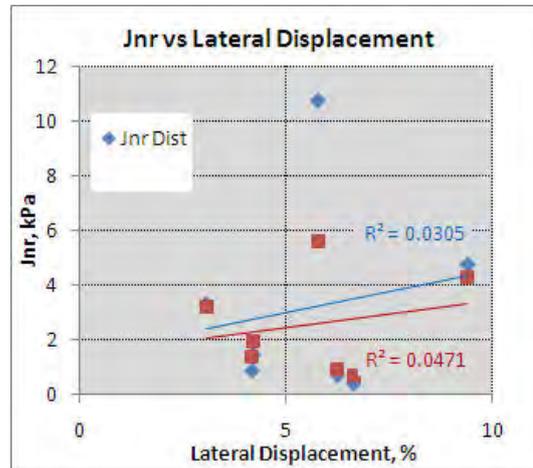
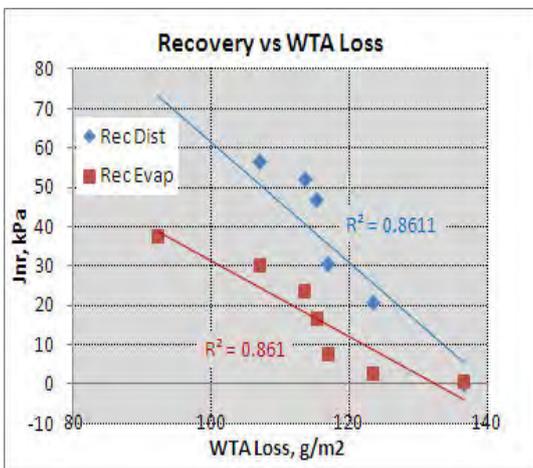


Fig 12. J<sub>nr</sub> vs Lateral Displacement



In trying to elucidate the above, correlations between micro surfacing WTA and LWT and residue parameters were analyzed. The empirical observation that Micro Surfacing abrasion loss diminishes with an increase in polymer content of the binder is verified by a strong correlation of the data (Fig 9). As a result, by plotting the J<sub>nr</sub> and the MSCR Recovery vs the WTA Loss, it appears that the MSCR Recovery is unable to distinguish between the two recovery methods but the J<sub>nr</sub> marginally does. We find a slightly better correlation between the J<sub>nr</sub> evaporation data than the J<sub>nr</sub> distillation. The graphs are shown as Figures 10 and 11.

By contrast, the LWT lateral and vertical displacement results show no relationship whatsoever with any of the binder properties. From the data it is pretty obvious that there must be mainly mix related parameters that govern the LWT performance and that the binder and its polymer content plays little or no role in how the displacements occur. This is somewhat unexpected, one would think that the J<sub>nr</sub> would show at least some influence, being a parameter designed to capture mainly the rutting susceptibility of a binder. But our data shows absolutely no correlation, as seen in Figure 12. Our belief is that it is the severity of the LWT test that is pushing the specimen behaviour beyond the failure zone where the effect of the binder can be quantified. The way it is performed, the test essentially measures the strength of the aggregate matrix and if the aggregate matrix is not performing adequate, the specimens will disintegrate regardless of the binder performance.

## 6.0 CONCLUSIONS AND SUMMARY

Seven different Micro Surfacing emulsions were prepared, containing SBR latex dosages between 0%

and 6%. Residues were recovered by the distillation and by the evaporation methods and all were tested for a number of rheological parameters. The same emulsions were used to prepare WTA and LWT Micro Surfacing specimens which were tested according to ISSA protocols. By analyzing the lab results, the following observations can be summarized.

Distillation and evaporation residue recovery methods for bitumen emulsions produce residues with very different properties. It appears that the evaporation procedure induces a higher degree of bitumen aging compared to the distillation. However, the distillation method yields polymer networks that exhibit higher elastic behaviour, at least when the SBR latex used contains a crosslinking agent. It is unclear which of the two recovery methods delivers binders that reflect more closely what happens in real life in the field. More research is needed in this direction. Distillation residues closer match the properties of the binder before its emulsification.

Elastic recovery of PMB emulsion residues vary widely with the recovery method. Using the MSCR test criteria, a 1% SBR emulsion residue can be characterized as elastic if it is obtained by the distillation method; by contrast a SBR dosage of 5% is needed to qualify as an elastic binder if the residue is recovered by evaporation.

Higher polymer content in a Micro Surfacing emulsion translates into lower WTA losses with satisfactory correlation values. WTA also correlates with MSCR Recovery and  $J_{nr}$ , marginally better with the evaporation residue  $J_{nr}$  values. No influence of the emulsion polymer content could be detected on the lateral and vertical displacement values for the LWT test.

Future research work is needed to better understand the full impact of the residue recovery methods of PMB emulsions and how it captures the behaviour of different emulsion and polymer types related to lab and field performance.

## 7.0 REFERENCES

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