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Re-refined Engine Oil Bottom: Detection and Upper Limits in Asphalt Binders and Seal Coat Binders

Technical Report 0-6881-R1

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16. Abstract

Many state departments of transportation have adopted the Superpave PG specification since the completion of the Strategic Highway Research Program in 1993. A much wider range of crude oil sources and binder modification techniques are being used now to produce asphalt binders. Although asphalt binders used these days still meet the requirements of the PG specification, many premature failures have been reported by many states. Texas Department of Transportation (TxDOT) initiated a study on re-refined engine oil bottom (REOB) in 2015. The objectives of this study were to establish REOB detection methods and recommend maximum allowable amount of REOB in asphalt binders and seal coat binders.

Based on existing literatures, researchers developed and verified scientific methods to detect and quantify the amount of REOB in both asphalt binders and seal coat binders using a handheld or a benchtop X-Ray Fluorescence (XRF) instrument. Furthermore, a comprehensive study was performed to define the impact of REOB on asphalt binders, asphalt mixtures, and seal coat performance. Multiple sources of binders, aggregates, and REOB (including recycled binders, PPA, and GTR) were used in the evaluation. Laboratory test results clearly indicated that the addition of REOB has detrimental effects on rutting, cracking, and seal coat adhesion properties. Not only should the current upper limit of 5 percent REOB in asphalt binders be kept, but an upper limit of 5 percent REOB in seal coat binders needs to be established. The implementation of these XRF tools and recommendations on the upper limits of REOB in binders will make pavements last longer as intended.

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RE-REFINED ENGINE OIL BOTTOM: DETECTION AND UPPER LIMITS IN ASPHALT BINDERS AND SEAL COAT BINDERS

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DISCLAIMER

This research was performed in cooperation with the Texas Department of Transportation (TxDOT) and the Federal Highway Administration (FHWA). The contents of this report reflect the views of the authors, who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official view or policies of the FHWA or TxDOT. This report does not constitute a standard, specification, or regulation.

This report is not intended for construction, bidding, or permit purposes. The engineer in charge of the project was Fujie Zhou, P.E. (Texas #95969).

The United States Government and the State of Texas do not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

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- Ryan Barborak
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- Robert Lee
- Jerry Peterson

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CHAPTER 1: INTRODUCTION

BACKGROUND AND OBJECTIVES

Superpave performance-grade (PG) binder specification was one of products from the Strategic Highway Research Program (SHRP). Since the completion of the SHRP in 1993, many state departments of transportation (DOTs) have adopted the Superpave PG specification. Meanwhile, both the crude oils and the formulation and manufacture of asphalt binders for pavement uses have changed significantly since 1993. A much wider range of crude oil sources are being used to produce asphalt binders now than then. Materials such as re-refined engine oil bottoms (REOB), polyphosphoric acid (PPA), bio-binders, and ground tire rubber (GTR) are increasingly being used to formulate and manufacture asphalt binders for pavement mixtures and asphalt seal coat binders. Although asphalt binders used in these days still meet the requirements of the PG specification, many highway agencies in United States are increasingly experiencing premature failures of newly constructed pavements. These failures include distresses such as low- and intermediate-temperature cracking and raveling, aggregate loss, and instances of total surface course loss within five years. Many pavement engineers express concerns on embrittlement and a lack of adhesion and tackiness of the asphalt binders. The Texas Department of Transportation (TxDOT) has become increasingly aware of these issues so that a new research on REOB was initiated to address it in 2015.

The main objectives of this study were to (1) establish REOB detection method, (2) evaluate the impact of REOB on asphalt binder properties, asphalt mixture properties, and seal coat performance, and (3) recommend the maximum allowable amount of REOB in asphalt binders and seal coat binders.

REPORT ORGANIZATION

This report is organized in six chapters. Chapter 1 provides a brief introduction, followed by a detailed literature review in Chapter 2. The REOB detection methods with a bench top X-ray fluorescence (XRF) and a handheld XRF for asphalt binders and seal coat binders are described in Chapters 3 and 4, respectively. Chapter 5 presents the impact of REOB on asphalt binder properties. Furthermore, the influences of REOB on asphalt mixture properties and seal coat performance are explained in Chapters 6 and Chapter 7, respectively. Finally, this report is concluded with a summary in Chapter 8.

CHAPTER 2: LITERATURE REVIEW ON REOB

REOB has been used to modify asphalt binders for a long time (Herrington 1992; Herrington et al. 1993; Herrington and Hamilton 1998). A recent report estimated that the paving industry is using nearly 160,000 tons of REOB in the United States per year (Asphalt Institute 2016). Recent studies have revealed that REOB is increasingly being used in Texas binders. Its negative impact on pavement performance was not reported until recent years. A very comprehensive literature review was conducted by the Asphalt Institute's Asphalt Binder Expert Task Group (2016). A total of 26 publications on REOB from 1980s to Jan. 1, 2015, were examined. The following sections will provide a synopsis of these studies and some of the latest studies on REOB.

REOB MANUFACTURING

REOB is one of several products obtained by refining the recovered engine oils in petroleum plants (see Figure 1). Several names have been used to denote REOB:

- Waste oil distillation bottoms (Herrington 1992).
- Engine oil residues (EORs) (Hesp et al. 2009b; Hesp and Shurvell 2010).
- Waste engine oils (WEO) (DeDene 2011; DeDene and You 2014).
- Used motor oil (Oliveira et al. 2013).
- Re-refined heavy vacuum distillation oils (RHVDO)/bottoms (D'Angelo et al. 2012, 2013).
- Vacuum tower asphalt bottoms (NORA 2014).
- Vacuum tower air extenders (VTAE) (Wielinski et al. 2014).
- REOB (Buncher 2014).
- Re-refined engine oil residues.
- Asphalt flux, asphalt extender, and asphalt blowdown.

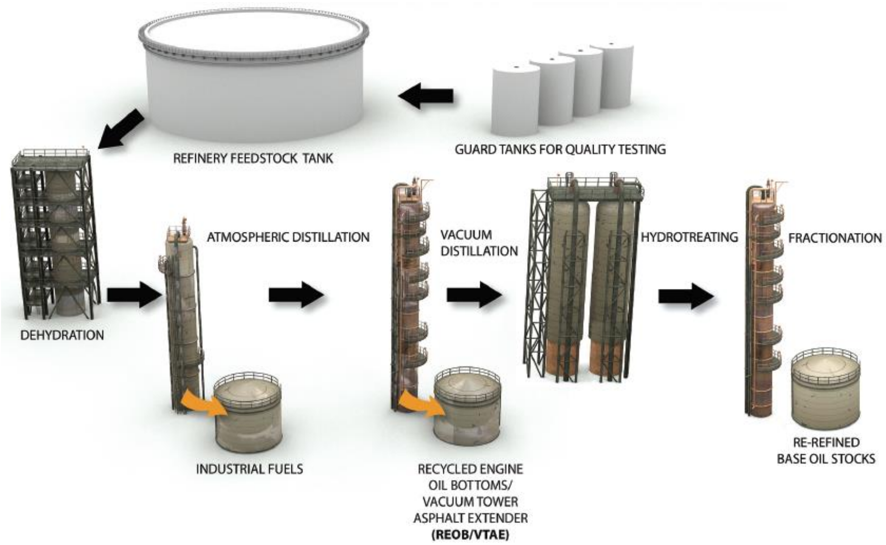


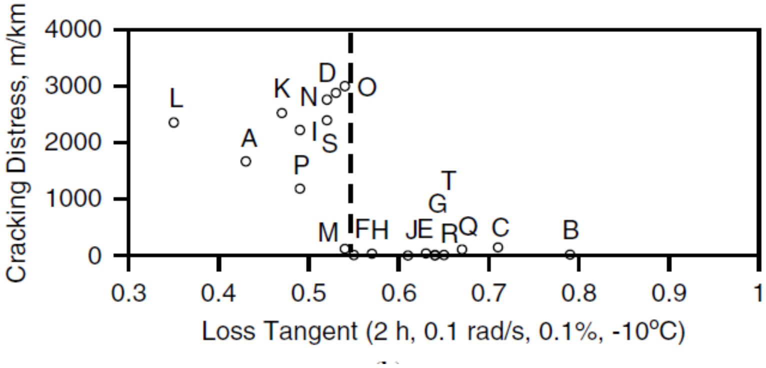
Figure 1. REOB in Manufacturing Process (Asphalt Institute 2016).

STUDIES EVIDENCING NEGATIVE EFFECT OF REOB

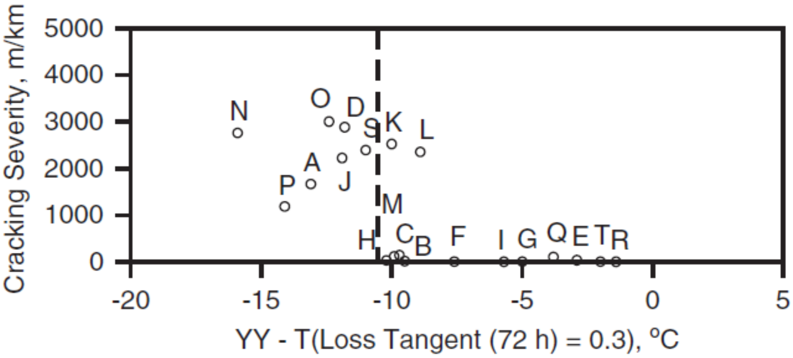
Effects of REOB on Binder Properties

Hesp et al. (2009b) evaluated 20 different asphalt pavement sections in eastern and northeastern Ontario, Canada, and found that nine of them had excessive premature cracks. The researchers measured low temperature grades and strain tolerances of binders obtained from each of these sections using bending beam rheometer (BBR) tests and double edge notched tensile (DENT) tests. They found that the binders associated with poorly performing pavement lost their low temperature grades and strain tolerance properties more significantly than the binders associated with well performing pavements. The researchers also showed that cracking severity was well correlated to low temperature grade measured from BBR tests after extended period (i.e., 72 hours) of conditioning and the crack tip opening displacement determined from DENT tests.

Hesp et al. (2009) obtained asphalt binder samples from the aforementioned 20 sections and measured their loss tangents at −10°C for 2 hours at 10-minute interval. The researchers found that most of time the loss tangent measured after two hours of conditioning could accurately separate the poorly performing pavements from the well performing ones [see Figure 2(a)]. Researchers also determined the critical low temperatures of these binders after 30-min and 72-hr conditioning using the loss tangent of 0.300 as the criterion, and showed it too could separate poorly performing pavements from other pavements the majority of time [see Figure 2(b)]. Researchers also confirmed from XRF and nuclear magnetic resonance tests that the binders used in poorly performing pavements contained zinc (Zn), the signature element of WEOs, and so concluded that the use of REOB in binder modification possibly degrades low temperature cracking resistance of binders (see Figure 2).



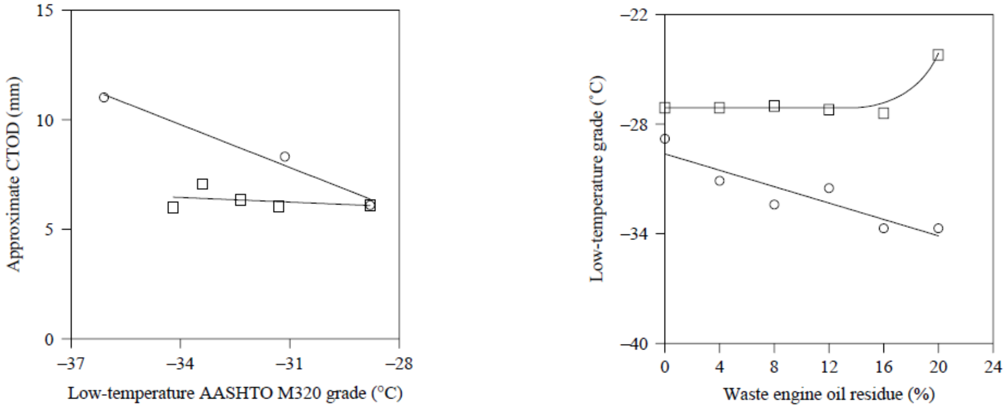
(a) With Loss Tangent after 2-hr. Conditioning



(b) With Low Temperature PGs Based on Loss Tangent = 0.300 after 72-hr. Conditioning

Figure 2. Correlations between Cracking Severity and Loss Tangent (Soleimani et al. 2009).

Hesp and Shurvell (2010) further evaluated the effect of REOB or waste EORs in asphalt on cracking properties of pavement in service. The researchers conducted the DENT tests on asphalt binder samples to determine their resistance to ductility and the extended BBR tests to determine their low-temperature PG. They observed that EORs have detrimental effects on low-temperature properties, as seen in Figure 3. As such, they attributed low-temperature cracks in pavements to the physical and chemical hardening that occurs due to EOR. Researchers applied XRF to compare the chemistry of virgin and reclaimed asphalt binder samples at different proportions. It was the first reported use of XRF technology in asphalt binders. Researchers found Zn in asphalt binder samples obtained from poorly performing pavements but did not detect it in samples obtained from well-performing pavements. Their analysis showed that typically 5–20 percent WEO were used in those pavements.



(a) DENT Test Results **(b) BBR Test Results**

Figure 3. Effect of WEO on Low Temperature Properties (Hesp and Shurvell 2010).

Note: Unmodified (Circles); WEO-Treated Asphalt (Squares)

Rubab et al. (2011) investigated the effect of REOB on oxidative hardening (i.e., aging) of asphalt cement using Fourier-Transform infrared (FTIR) spectroscopy tests. Using blends doped with three different percentages of EORs, the researchers showed that both the instantaneous and the steady oxidation rates increase with the increase in EOR dosage based on absolute value of carbonyl area. Researchers attributed this increase in oxidation rates to the presence of a large amount of metal catalysts (e.g., iron [Fe], copper [Cu], chromium) and/or oxidized engine oil components. They also provided evidence of the impact of REOB on aging using extended BBR as shown in Figure 4. However, D’Angelo et al. (2012) later showed that the EOR-blended binders have the same aging rate as the base asphalt binder based on the increase in the value of carbonyl area due to EOR.

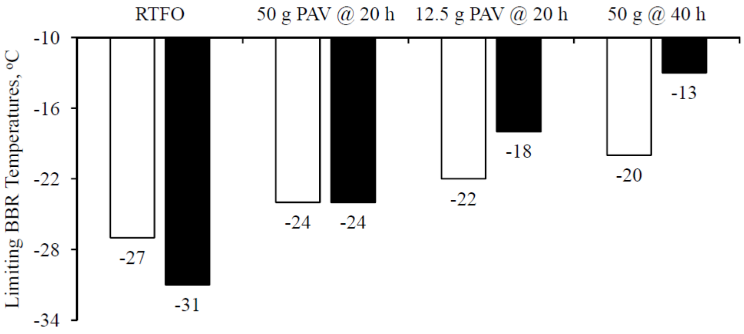


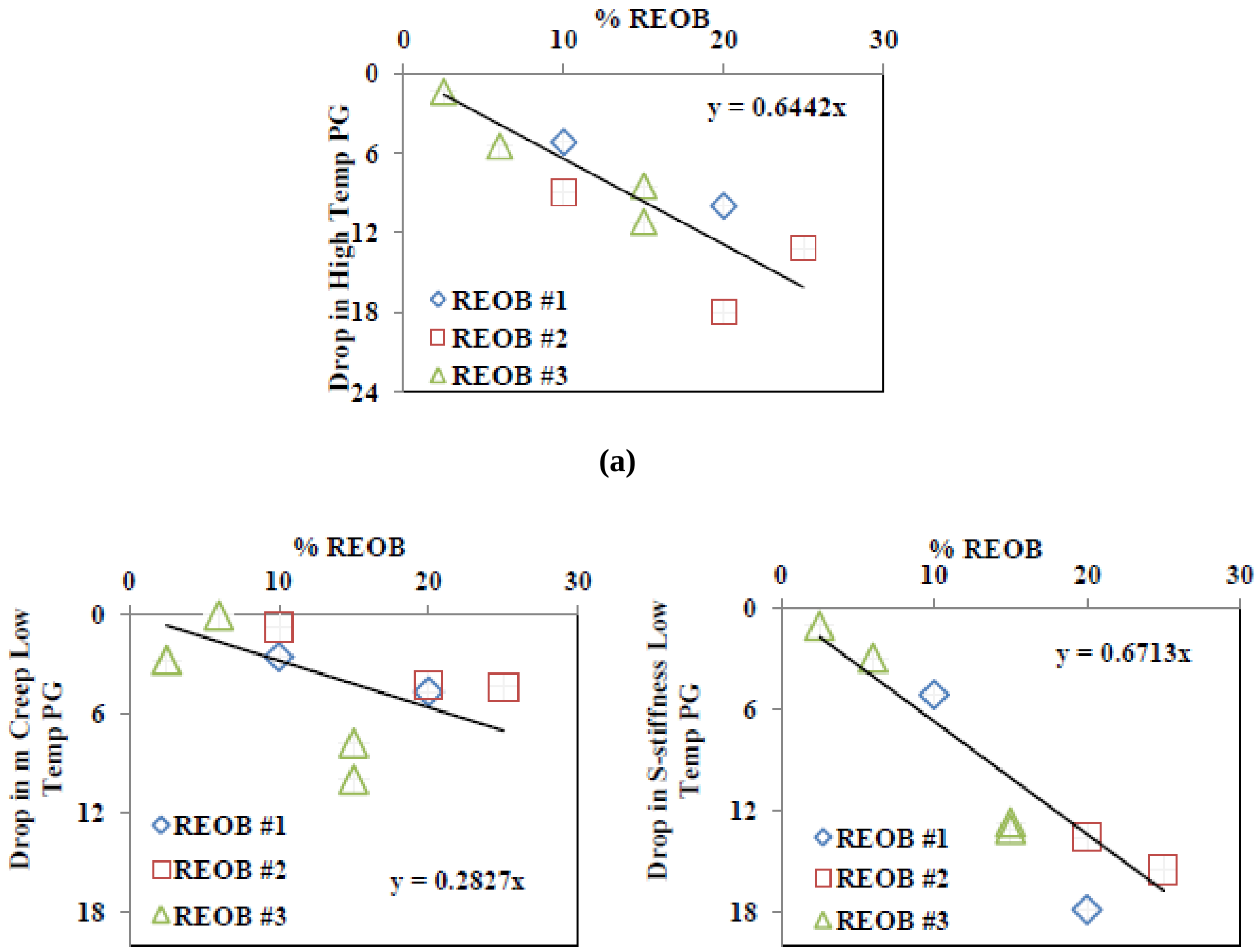
Figure 4. Effect of EOR on Limiting Low Temperature (Rubab et al. 2011).

Note: Cold Lake 200/300 Binder (Blank); 80/100 Binder + 20%EOR (Filled)

Reinke et al. (2014) investigated factors impacting performance of binders blended with additives for reducing low temperature properties of asphalt binders and their impact on mix performance. The researchers found that non-asphaltic materials added to conventional binders do not seem to age well; the impact of non-asphaltic blend components seems to have more effect on fatigue properties than low temperature cracking. They also concluded that the use of excessive levels of paraffinic oil-derived additives produces properties that might impact fatigue cracking performance; the use of additives containing five or higher of paraffinic-derived oils produce binders that do not age well at low temperature.

Planche (2014) evaluated both lab and field performance of mixtures containing REOB-modified asphalt at the Western Research Institute. The research team investigated the effects of long-term aging on REOB-modified binders using infrared-based chemical analysis and atomic force microscopy (AFM) imaging. They found that REOB changed the structure of binders in nano-/micro-scale and aging behavior of base binders.

Gibson et al. (2015) studied influence of three sources of REOB on different binder blends in terms of the high temperature PG, the creep stiffness-based low temperature PG, and the creep slope-based low temperature PG. They found that it required at least 9 percent REOB to reduce the high temperature PG and the stiffness-based low temperature PG by one grade but at least 21 percent REOB to drop the m-based low temperature PG by one grade (see Figure 5). Results further showed that binder type, REOB source, REOB dosage, and the binder source each impacted the extent of the variation of PG binder grade. They also found that excessive use of REOB can make binders more susceptible to cracking.



(a)

(b)

Figure 5. Effect of Source of REOB on Binder PG (Li et al. 2017).

Bennert (2015) studied the effects of REOB on low temperature cracking properties of asphalt binders in terms of the difference between the critical temperatures ($\Delta T_c = T_{c,s-\text{value}} - T_{c,m-\text{value}}$) estimated from creep stiffness (S-value) and creep relaxation (m-value) data of BBR tests, respectively. Researchers showed that the effect of REOB in asphalt binder is clearly evident in ΔT_c compared to that in m-value, and more so when it is aged for longer periods (see Figure 6). They also proved that the stiffness-based tests cannot discriminate unmodified binders from REOB-modified binders.

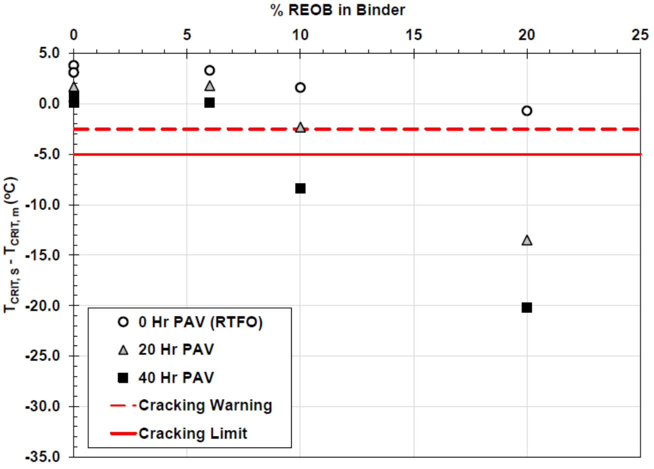
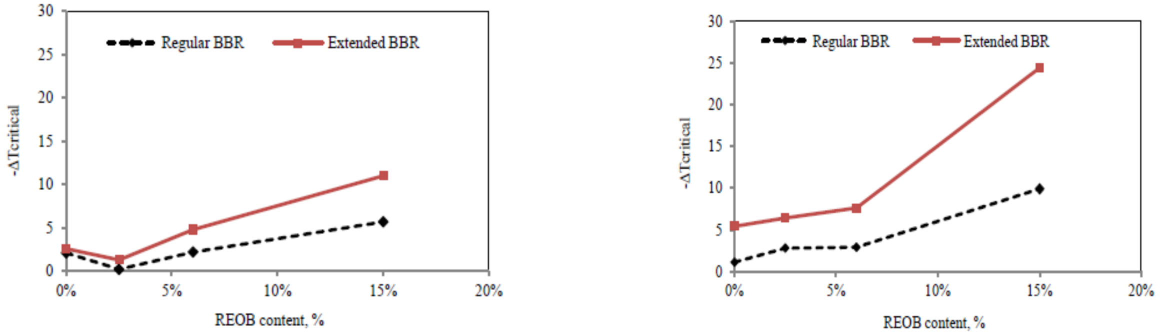


Figure 6. Effect of REOB on ΔTc (Bennert 2015).

Li et al. (2017) evaluated a group of asphalt binders of the same PG but a wide range of REOB contents. The researchers concluded that the most practical rheological indicator of the possible presence of a considerable quantity of REOB was the $\Delta T_c = T_{c,s-value} - T_{c,m-value}$ obtained from both regular and extended BBR tests (see Figure 7). They mentioned that when a binder exhibited a large ΔT_c, it was associated with larger differences in performance loss depending on the binder tests and to a lesser extent in the mixture test. Similarly, they mentioned that ΔT_c performance disruption was made worse by oxidative aging (see Figure 7). They also found that an increase in REOB content would increase moisture susceptibility.



(a) 20 hr. PAV-Aging **(b) 40 hr. PAV-Aging**

Figure 7. Effect of REOB and Aging on ΔTc (Li et al. 2017).

The asphalt industry itself has recognized the need for uniform specifications for REOB (or VTAE) recently. As such, in 2015, the National Oil Recyclers Association (NORA) (2014) issued two American Society for Testing and Materials specifications for VTAE, one of those for VTAE used in the formulation of asphalt paving and asphalt roofing materials. These specifications set limits for flash and fire points, change in mass due to short-term aging, solubility, and viscosity of REOB as shown in Table 1. However, meeting these requirements alone might not be sufficient to guarantee good quality of binders as claimed by many research studies.

Table 1. Requirements for VTAE or REOB (NORA 2014).

Test	Value
Flash Point, Cleveland Open Cup, min, °C [°F]	>232 [450]
Mass Change, Rolling Thin Film Oven Test, %w/w max	1.0
Solubility in Trichloroethylene, min, %	98.0^A
Viscosity, 60°C [140°F], max, cP	5000
A = Solubility of less than 98.0% is acceptable provided the final blended product meets the solubility requirements in the specifications.	

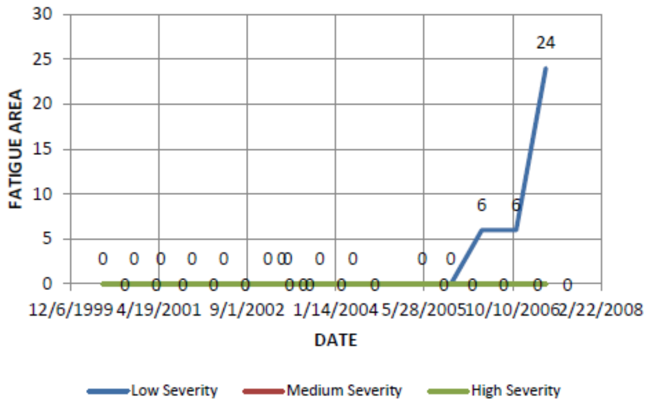
Effects on Asphalt Mixture Field Performance

Hesp and Shurvell (2010) published a study investigating the effects of re-refined vacuum tower bottoms (RVTB) on cracking of pavements in service. The authors had evaluated the effect of RVTB on physical hardening and loss of strain tolerance for laboratory-aged asphalt binders and concluded that RVTB would cause increased cracking. For in-service pavements that tested positive to the presence of Zn, the authors concluded that observed premature and excessive cracking failures in Ontario pavements was related to the presence of RVTB. Their conclusions are based on visual distress surveys of 15 poorly performing (cracked) pavements that showed levels of Zn in the recovered asphalt from XRF. They also found that of the 11 good performing projects included in the study, none had contained Zn.

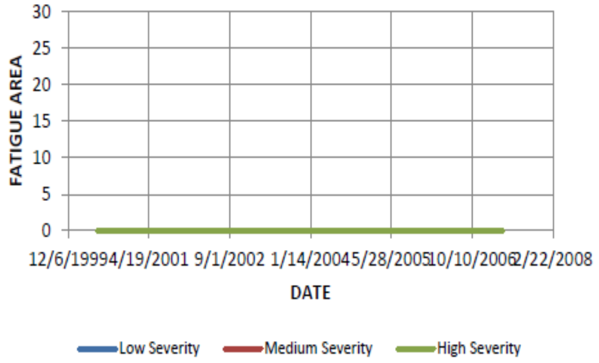
Bennert et al. (2015; 2016) showed binder fatigue tests correlated well with the Texas Overlay Test (OT) and were sensitive to REOB dosage. Researchers also concluded that REOB dosage had an impact on performance, but magnitude was not the same for each REOB source. They also found that at a lower (e.g., 6 percent) REOB dosage, there were differences between the three REOB-modified and neat asphalt binders. Furthermore, the differences became larger as the REOB dosage increased. They attributed these differences to accelerated hardening of the asphalt binder when aged. They concluded that at low dosage the addition of REOB may be used with no detrimental effects. Researchers cautioned that the REOB source, and just as important, asphalt binder source should be evaluated together prior to use to ensure the compatibility between the materials.

Li et al. (2017) could not make conclusive observations on the effect of REOB on low-temperature relaxation, strength, and fracture measured with thermal stress restrained specimen test. However, they could see that the strength of the mix with 15 percent REOB decreased significantly when aging.

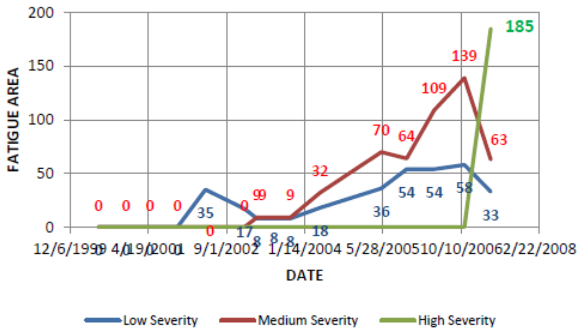
Reinke et al. (2015) re-investigated three sections on MnRoad, which was built in 1999: Cell 33 with PG 58-28, Cell 34 with PG 58-34, and Cell 35 with PG 58-40. They tested the three binders and found that the PG 58-40 binder had REOB in it. Figure 8 shows transverse cracking development in the field. It is obvious that Cell 35 with PG 58-40 modified with REOB had the poorest performance, although it has the lowest PG low end.



(a) With PG 58-28



(b) With PG 58-34



(c) With 58-40

Figure 8. Field Performance of Test Sections at MnRoad Cell 33 (Reinke et al. 2015).

STUDIES EVIDENCING NO DETRIMENTAL EFFECT OF REOB

The Asphalt Institute's Asphalt Binder Expert Task Group (2016) found that half out of 26 published papers on REOB until Jan. 1, 2015, did not find a strong evidence of detrimental effect of REOB on pavement performance. Some even reported beneficial effect of REOB instead. The section presents brief synopses of some of these studies, including a few new papers published since then.

Herrington (1992) investigated the potential for use of REOB or vacuum distillation bottoms produced during the re-refining of waste automotive oils as extenders for bitumens used in pavement construction. In terms of chemistry, Herrington mentioned that lead, magnesium, chromium, cadmium, nickel, vanadium (V), and Fe are the key elements of such residues. The researcher investigated simple rheological properties, including aging properties of the extended blends. The researcher found considerable variation in viscosity of REOB batches collected over a period of about 13 months. The researcher also observed that the temperature susceptibility of the base asphalt was reduced when up to 10 percent REOB was added. The researcher pointed out that variation in bitumen-REOB blend properties might pose difficulties for meeting roading authority specifications. However, the researcher also observed that oxidative hardening properties of the blends prepared with 10–20 percent REOB were similar to one another and to those of standard bitumen at least unto the highest temperatures likely to be experienced in practice.

D'Angelo et al. (2012) studied performance characteristics of asphalt binders modified with REOB or RHVDO at several different concentrations. Researchers selected asphalt binders from two different sources and blended them with one RHVDO from two different sources at several different concentrations (0–20 percent). Researchers ran chemical (saturates, aromatics, resins and asphaltenes [SARA]) tests on RHVDO, base binders, and their blends to study chemical changes that occur due to such blending. They also conducted rheological tests to measure the physical properties at different conditions of aging. They found that the selected two RHVDO were predominantly made up of polar aromatics and saturates with a small percentage of asphaltenes. However, the concentrations of polar aromatics and saturates in REOB were half as much as that in base binders. Moreover, the asphaltenes present in base binders lose associations due to saturates in RHVDO, thereby inducing embrittlement in binders (see Figure 9). D'Angelo et al. (2012) found that effect of RHVDO on high, intermediate, and low temperature properties of asphalt binders depends on the source of both RHVDO and base binders. In particular, this study showed that higher concentration of RHVDO (even at 20 percent) and longer duration of aging (35 hours) neither increase the growth rate of oxidation or aging, meaning the growth rate of aging is controlled by the base binder instead (see Figure 10).

D'Angelo et al. (2013) later evaluated the performance characteristics of asphalt mixes produced with RHVDO-blended binders. High-temperature rutting tests (Hamburg Wheel Tracking Tests [HWTT] and Flow Number) revealed that asphalt mixes produced with RHVDO-blended binders performed as well as or even better than the control mixes with similar binder stiffness. However, American Association of State Highway and Transportation Officials (AASHTO) T283 tests could not discriminate the stripping potential of mixes with up to 6 percent RHVDO. Furthermore, disk-shaped compact tension tests and beam fatigue tests demonstrated that mixes produced with RHVDO-blended binders performed as well as or better than the corresponding control mixes both at intermediate and low temperatures.

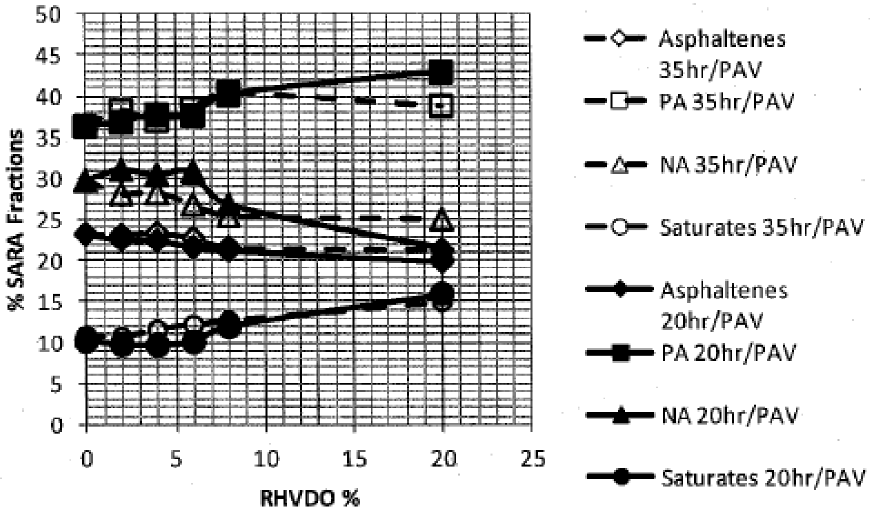


Figure 9. SARA Fractions in REOB-Modified Binders (D'Angelo et al. 2012).

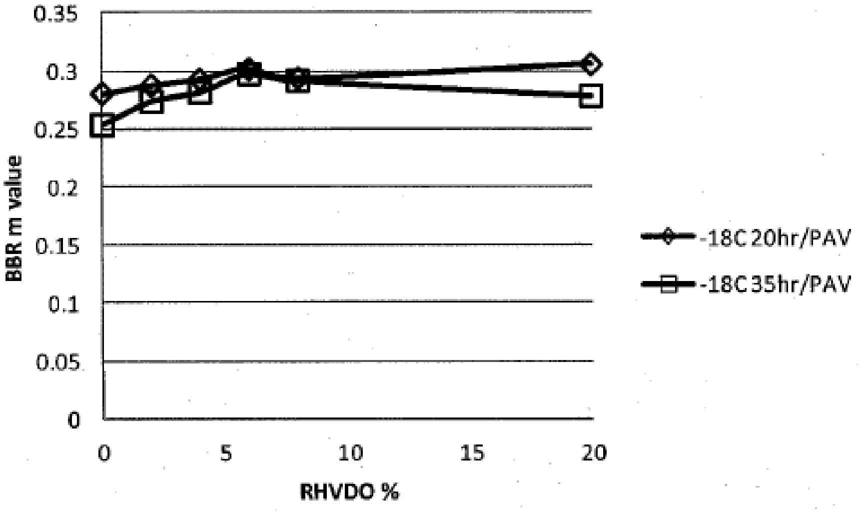


Figure 10. BBR Test Results in REOB-Modified Binders (D'Angelo et al. 2012).

Golalipour et al. (2013; 2014) investigated the effects of oil modification on low temperature cracking resistance of binders. For this, researchers measured creep stiffness from BBR tests and non-linear thermal contraction rate from glass transition tests and then used them to estimate thermal stresses at different cooling rate. Researchers conducted single-edge notch beam tests to measure fracture properties of binders. The study reported that binders modified with REOB actually improve cracking resistance in binders by increasing failure energy. This study suggested that such modification makes binder more suitable for low temperature applications even after different aging levels.

Wielinski et al. (2014), at the Heritage Research Group, conducted extensive research on the use and impact of REOB for the Illinois Department of Transportation in 2014. Researchers conducted chemical analysis of asphalt blended with REOB and their effect on hot-mix asphalt (HMA) mixture performance. Researchers found that, overall, introducing REOB into an asphalt binder at a rate of 9 percent, sufficient to convert PG from PG64-22 to PG58-28, does not compromise mixture stiffness or aging. In this particular case, this addition actually enhanced the resistance to moisture damage and resistance to fatigue damage.

Mogawer et al. (2015) studied the impact of aging on chemical and performance characteristics of REOB-modified asphalt binders and mixtures. In that particular study, researchers blended two different REOB and one extender oil with three straight run binders separately. They discussed a simple method to determine the maximum and minimum amount of REOB to reach the target high- and low-temperature PG. Researchers did not find significant difference between fracture properties of mixtures prepared with unmodified and mixtures prepared with REOB-modified binders, as shown in Figure 11.

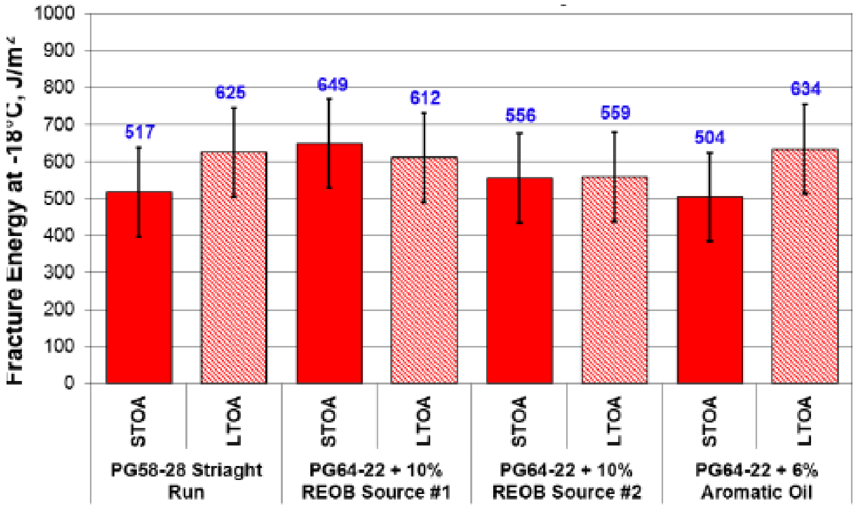


Figure 11. Fracture Energies of Mixtures (Mogawer 2015).

REOB DETECTION STUDIES

In last several years, a few studies attempted to develop methods for detecting the presence of REOB and determining its content in asphalt binders. Hesp and Shurvell (2010) used a portable energy dispersive X-ray fluorescence (EDXRF) and found that Zn is a signature element of REOB-modified binder. D'Angelo et al. (2012) also conducted inductively couple plasma atomic emission spectrometry tests and found that presence of higher than normal amount of calcium (Ca), phosphorus (P), Zn, and Fe are strong proof of binder modification with REOB. At the Federal Highway Administration (FHWA), Arnold (2014) measured concentrations of several elements in asphalt binder samples using a high power benchtop EDXRF instrument and found that binders modified with REOB almost always contained Ca, Cu, molybdenum (Mo) in addition to Zn. Furthermore, the FHWA research team conducted XRF tests of 13 different REOB, 13 different GTRs, 5 different automotive lubricants, and 1208 binder samples received from 38 agencies from around the country, and measured the concentration of heavy metals in them. Test results showed that both REOB and automotive lubricants contained P, sulfur (S), Ca, Fe, Cu, Zn, and Mo. The results also showed that unmodified binders contained Fe, Mo, and S while GTRs predominantly contained Zn only. The team also showed that the composition of REOB varies, not only between different producers but also within samples taken from the same producer at different times, as previously suggested by Herrington et al. (1992). Based on the test results, the FHWA researchers (Arnold and Shastry 2015) recommended estimating REOB content in a unknown sample using the calibration curves obtained by plotting Ca, Cu, Mo, and Zn concentrations versus the known dosages of REOB. But since REOB and binder sources directly influence these concentrations, it is imperative to select a representative standard before such estimation. But this study did not address this issue effectively.

In 2016, TxDOT's researchers (Barborak et al. 2016) presented one method to detect REOB in asphalt binders using XRF analysis. Unlike FHWA's research team, TxDOT's research team used wavelength dispersive X-ray fluorescence spectroscopy for that particular study. The TxDOT researchers clearly showed that intensities of P, Mo, Zn, Cu, Ca, and K detected by XRF spectrometer can be used to determine the presence and the percentage of REOB in asphalt binders. They identified four calibration standards based on V versus S intensities. They also showed that when a specification limit of 5 percent REOB was considered, the maximum error was 5.7 percent if the REOB and binder were known, and 21.3 percent if only the REOB were known. If neither the REOB nor binder was known, the maximum error would rise to 46.0 percent.

CURRENT STATE PRACTICE ON THE USE OF REOB IN ASPHALT BINDERS

Since the use of REOB in asphalt binder modification was not extensively revealed until recently, only limited studies have been performed on the impact of REOB on the performance of asphalt binders, asphalt mixtures, and asphalt pavements. As such, DOTs around the country are facing a dilemma as to whether to completely ban the use of REOB or set a maximum allowable percentage in binder modification. To this end, several northeastern and midwestern state transportation agencies have issued an edict that required all suppliers of PG binders certify that the binders supplied for use on their projects do not contain REOB at all. The increasing tendency of banning the use of REOB in pavements could be an over-reaction to the problems encountered, because it has been shown that small levels of modification have been used since the 1980s and there are not many reports that justify such bans. Asphalt suppliers claim that complete ban of such products in pavements might force them to use other additives that might potentially make binders more expensive, potentially carcinogenic, and even degrade the overall quality of binders (Bouldin 2014). The suppliers also point out that REOB cut greenhouse gas emissions by 85 percent relative to asphalt produced from crude oil. Alternatively, three southern and southeastern state DOTs, including TxDOT, have set the maximum allowable percentage of REOB at 5 percent. Bennert et al. (2016) summarized current state of regulations on the use of REOB as follows:

- Northeast United States: Connecticut, Massachusetts, New Hampshire, New York, Rhode Island, and Vermont.
- Midwest United States: Colorado, Illinois, and Michigan.
- South and southeast United States: Texas, South Carolina, and Georgia (limits to ≤5 percent).

SUMMARY AND CHALLENGES

REOB has been used to modify asphalt binders for a long time. The consequences of higher levels of REOB have been observed both in laboratory testing and in recent premature pavement failures:

- **Cracking:** Hesp et al. first reported the early cracking problem of asphalt mixtures containing REOB in Canada (2009a). Hesp and Shurvell (2010) reported that 11 pavements with asphalt binders modified by REOB showed more cracking than those without REOB in Ontario, Canada. The Vermont Department of Transportation also reported raveling and cracking problems of pavements with asphalt mixtures containing REOB (Ahearn 2015). Reinke et al. (2015) reported that pavements constructed with REOB showed more cracking on MnRoad and Olmsted County Highway 112.
- **Stripping:** Anti-strip materials are also performing differently in mixes than in past paving seasons. In some mixes, the use of lime has made the moisture susceptibility worse (whether this is caused by the use REOB or PPA is open to investigation).
- **Early Aging:** Several districts have reported concerns about early raveling of permeable friction course mixtures, and in some cases, the mixes have lost their black color prematurely and look extremely aged after only a few weeks in service.
- **Rutting and Moisture Damage:** In the laboratory and in trail batches, mixes have been found to be substantially more susceptible to moisture than in the past. Mixes that have traditionally passed TxDOT performance criteria easily are now failing the HWTT and other performance tests.
- **Other Issues:** Some unexplained failures of hot-pour asphalt seal coats were reported in several districts in Texas too.

Therefore, it is important to understand the basic properties of REOB and evaluate their potential effects on binder, mix properties, and seal coat performance.

CHALLENGES OF ADDRESSING THE REOB PROBLEM

There are at least three challenges when dealing with the REOB problem, as described below:

- **Accurate determination of REOB content both in the laboratory and field**
  Accurate determination of REOB/PPA content in the asphalt binders could be a challenge because REOB itself varies significantly from one source to another. Additionally, asphalt binder itself varies from one supplier to another. Thus, various sources of REOB and asphalt binders must be considered in this study to develop an accurate standardization or calibration curve for REOB content in the laboratory.

  For field applications, handheld XRF unit is preferred. However, handheld XRF units are an energy dispersive system, which is different from the wavelength dispersive system being used in the TxDOT laboratory. Thus, there is a challenge between XRF systems (energy dispersive vs. wavelength dispersive) in terms of the accuracy.

- **Maximum allowable amount of REOB in asphalt binders**
  It may be true that the impact of REOB/PPA on asphalt binder properties depends on both the sources of REOB and asphalt binder itself. Thus, significant amount of laboratory tests should be performed to determine the maximum allowable REOB amount for uses in HMA binders through both binder and mixture tests.

- **Maximum allowable amount of REOB in seal coat binders**
  Compared to asphalt binders, impact of REOB on seal coat performance has not been well investigated. It is more challenged when dealing with seal coats because there is no laboratory procedure well established for evaluating seal coat performance.

CHAPTER 3: REOB DETECTION METHODS FOR ASPHALT BINDERS

To reduce or avoid the negative impact of REOB on pavement performance, some state transportation agencies either completely banned the use of REOB in asphalt binders or set an upper limit on the REOB use (Bennert et al. 2016). Thus, it is essential to develop a method for precisely quantifying REOB content in asphalt binders. This chapter addresses this issue. The following sections first introduce the XRF briefly and then describe the new methods.

INTRODUCTION OF X-RAY FLUORESCENCE

XRF spectrometry is an analytical method to determine the chemical composition of materials. The materials can be in solid, liquid, powder, filtered, or other form. XRF can also sometimes be used to determine the thickness and composition of layers and coatings. The method is fast, accurate, and non-destructive, and usually requires only a minimum of sample preparation. The applications are very broad and include the metal, cement, oil, polymer, plastic, and food industries, along with mining, mineralogy and geology, and environmental analysis of water and waste materials. XRF is also a very useful analysis technique for research and pharmacy. The precision and reproducibility of XRF analysis is very high. Very accurate results are possible when good standard specimens are available, but also in applications where no specific standards can be found. The measurement time depends on the number of elements to be determined and the required accuracy, and varies between seconds and minutes. The analysis time after the measurement is only a few seconds.

XRF Instruments

The basic concept for all spectrometers is a source, a sample, and a detection system. The source irradiates a sample, and a detector measures the radiation coming from the sample. In most cases the source is an X-ray tube, although alternative types exist.

Spectrometer systems are generally divided into two main groups: energy dispersive system (EDXRF) and wavelength dispersive system (WDXRF). The difference between the two systems is found in the detection system:

- EDXRF spectrometers have a detector that is able to measure the different energies of the characteristic radiation coming directly from the sample. The detector can separate the radiation from the sample into the radiation from the elements in the sample. This separation is called dispersion. Most handheld XRF units are energy dispersive units.
- WDXRF spectrometers use an analyzing crystal to disperse the different energies. All radiation coming from the sample falls on the crystal. The crystal diffracts the different energies in different directions, similar to a prism that disperses different colors in different directions.

Table 2 shows the comparison of EDXRF and WDXRF spectrometers and their advantages and disadvantages.

Table 2. Comparison of EDXRF vs. WDXRF Technologies.

Character	EDXRF	WDXRF
Elemental range	Na to U (sodium to uranium)	Be to U (beryllium to uranium)
Detection limit	Less optimal for light elements Good for heavy elements	Good for Be and all heavier elements
Sensitivity	Less optimal for light elements Good for heavy elements	Reasonable for light elements Good for heavy elements
Resolution	Less optimal for light elements Good for heavy elements	Good for light elements Less optimal for heavy elements
Costs	Relatively inexpensive	Relatively expensive
Power consumption	5 to 1000 W	200 to 4000 W
Measurement	Simultaneous	Sequential/simultaneous
Critical moving parts	No	Crystal, goniometer

Additionally, XRF instruments, based on the mobility, can be divided into three groups: handheld, portable, and benchtop (or lab model). The benchtop XRFs are often designed to be used for lab analysis with complex software and to provide accurate results (auto-sampler, optimized excitation, and report generation). However, bringing binder samples from each mixture production facility and construction site to the laboratory is not always practical. It is necessary to have units that can detect REOB and PPA levels in the field itself. Therefore, there are options that can be easily transported and used in the field. They are referred to as handheld and portable units. The handheld and portable XRF are easy to use and are mainly used for screening, although they can give accurate results when used by a knowledgeable operator. For this project, a lithium-battery powered handheld EDXRF (Thermo Fisher Niton XL3t 955 Ultra Analyzer) and a high power benchtop sequential WDXRF (Rigaku Supermini200) were used.

XRF Measurements

XRF is very sensitive technique and samples must be clean. Even fingerprints on a sample can affect the result of the analysis. For accurate results, the spectrometer (for example, the kV settings of the tube or the detector settings) is tuned to the elements to be analyzed. Bad setting can lead to poor results. In EDXRF, a whole element spectrum is measured simultaneously and the area of a peak profile determines the concentration of an element. Measuring the height of the peak profile is an alternative, but a lot of information would be lost because the area of a peak profile is less sensitive to noise than the height of the same peak. In WDXRF, it is common practice to measure only at the top of the peak profile. The positions of the peaks are known and measuring only at the top position gives the best accuracy and the lowest measuring time. For this study, both the peak and the background were analyzed for even better accuracy.

XRF Analyses

After a sample is measured, it is analyzed in two steps: qualitative analysis followed by quantitative analysis. Qualitative analysis determines which elements are present and their net intensities from the measured spectra. In many routine situations, the elements in the sample are known and only the net intensities need to be determined. The net intensities are used in quantitative analysis to calculate the concentrations of the elements present.

EDXRF and WDXRF often use slightly different methods for qualitative analysis. In EDXRF, the area of a peak gives the intensity, while in WDXRF, the height of the peak gives the intensity. Both methods would work for EDXRF and WDXRF, but both have their specific advantages and disadvantages.

Quantitative analysis is basically the same for EDXRF and WDXRF. The only difference is that the area of a peak gives the intensity in EDXRF, while the height of a peak gives the intensity in WDXRF. The same mathematical methods can be used to calculate the composition of samples.

In quantitative analysis, the net intensities are converted into concentrations. The usual procedure is to calibrate the spectrometer by measuring one or more reference materials. The calibration determines the relationship between the concentrations of elements and the intensity of the fluorescent lines of those elements. Unknown concentrations can be determined once the relationship is known. The intensities of the elements with unknown concentration are measured, with the corresponding concentration being determined from the calibration.

PREVIOUS XRF WORK ON DETECTING REOB

Both handheld and benchtop XRF instruments have been used to detect REOB. As mentioned previously, Hesp and Shurvell were among the first researchers who used a handheld EDXRF unit to detect the presence of REOB in asphalt binder (Hesp and Shurvell 2010). FHWA researchers used a benchtop EDXRF unit to detect both the presence and content of REOB in asphalt binders (Arnold 2014; Arnold and Nelson 2015; Arnold and Shastry 2015). They tested more than 1200 asphalt samples sent from different states were tested. Based on the massive work, they proposed a flowchart to determine whether or not REOB and GTR exist in asphalt binders. Recently, Heritage Research Group studied REOB with WDXRF (Wielinski et al. 2014). TxDOT used a WDXRF to detect REOB (Barborak et al. 2016). As the part of this project, researchers verified and used the detection method proposed by the FHWA researchers for this project.

XRF TEST, RESULTS, AND ANALYSES

The literature review in Chapter 2 indicated that selecting correct calibration standards is the key to accurate estimation of REOB. TxDOT researchers suggested using S and V intensity plots of all known and unknown samples to select correct calibration standards (Barborak et al. 2016), but no systematic method for selecting calibration standards was proposed. Researchers recognized the need to identify the sources of asphalt binder and REOB first and then identify a calibration standard to make the estimation of REOB content in asphalt binders more accurate. The following sections will present two methods developed for detecting REOB content in asphalt binders: one using benchtop WDXRF readings and the other using handheld EDXRF readings.

Selected Materials

For this part of the project, researchers selected several sources, grades, and dosages of asphalt binders and REOB to prepare samples required to develop calibration standards for detecting REOB levels in asphalt binders:

- 6 REOB: 6 different sources—denoted as R1 to R6.
- 20 asphalt binders (see Table 3):
  - 10 different sources—denoted as A to J.
  - 5 different PGs.
  - 1 penetration grade (0-Pen or Hard Pen).

Table 3. Sources of Asphalt Binders Used in this Study.

Source	PG	Notation
#1	64-22	A6422
#2	64-22	B6422
	64-28	B6428
	70-22	B7022
	70-28	B7028
#3	64-22	C6422
	64-28	C6428
	76-22	C7622
#4	64-22	D6422
#5	64-22	E6422
	76-22	E7622
	Hard Pen (0-Pen)	E-HP
#6	76-22	F7622
#7	64-22	G6422
	70-22	G7022
	70-28	G7028
	76-22	G7622
#8	64-28	H6428
#9	70-22	I7022
#10	64-22	J6422

XRF Instruments Selected This Study

At this study, researchers chose to use the benchtop sequential Rigaku Supermini 200 WDXRF spectrometry instrument (50kV, 200W, 5eV) and a handheld portable Niton XL3t Ultra Analyzer EDXRF spectrometry instrument (max 50keV, max 40 μA). Figure 12 shows the instruments. The selected benchtop instrument can detect wavelengths of secondary X-ray dispersed from fluorine (F) to U in a vacuum, helium, or air atmosphere at 36.5°C using two detectors: a P10-gas-filled proportional detector for the elements with longer wavelengths and a scintillation detector for the elements with shorter wavelengths. This instrument counts the number of times each selected element is detected and records them in terms of kcps. Since the vacuum can potentially swallow the heated binder/REOB blends, thereby contaminating the X-ray chamber and damaging the instrument, this study used an ultra-pure helium atmosphere for all the measurements.

EDXRF spectroscopy works very similar to WDXRF except that it uses energy instead of wavelength to detect the presence of elements in a sample of interest. The selected handheld instrument can detect more than 25 elements from aluminum to U by using a high-performance semiconductor. This instrument measures the concentration of each detected element in parts per million (ppm) instead of intensity. Since these types of instruments can be powered with a battery and weigh only a few pounds, they can be carried to remote pavement sections, allowing instant detection of REOB.

Benchtop WDXRF:

Supermini200

Handheld EDXRF:

Niton XL3t Ultra Analyzer

Figure 12. Selected XRF Spectroscopy Instruments.

Sample Preparation

Binders were first heated at mixing temperatures in a conventional oven and then doped with different dosages of REOB. Since REOB are already in the liquid state at room temperature, they were directly added to the heated asphalt binder without any heating and then stirred with a wooden spatula. The blends were heated again at their mixing temperatures for five minutes and then stirred with the wooden spatula thrice in a row to make them homogeneous.

Then, 9.0±1.0 grams of these blends were poured into plastic cups that measured 39.4 mm in outside diameter, 23.1 mm in height, and 31.0 mm in internal aperture. The cups were sealed with 6 μm thin films of polypropylene at the bottom end before pouring the blends into the cups. Vented caps were snapped on the other ends of these cups after specimen temperature cooled down to room temperature. Figure 13 illustrates the major steps of this process.

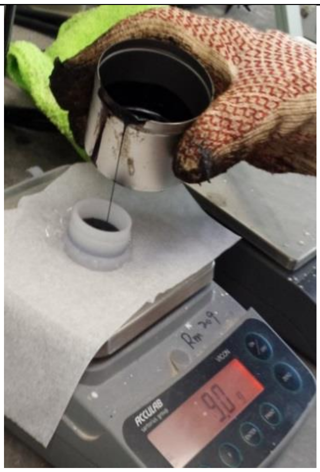
		
Sample Cup	**Placing the film on one side**	**Before pouring binder**
		
Sample Decantation	**After pouring the sample**	**Snap-On Cap**

Figure 13. Sample Preparation for XRF Tests.

A total of 384 asphalt binder/REOB blends were prepared by blending 163 different binders with 2.5, 5, 10, and 20 percent REOB by total weight of blends, as detailed below:

- 2.5%REOB + 97.5% Binder.
- 5.0%REOB + 95.0% Binder.
- 10.0%REOB + 90.0% Binder.
- 20.0%REOB + 80.0% Binder.

Two specimens were prepared for each sample used in this study, resulting in a total of 800 calibration specimens (2 × 15 unmodified binder specimens and 2 × 384 REOB-modified binder specimens). An additional 8 blends were also prepared by blending random sources of binders with random sources of REOB at 2.0 percent, 7.0 percent, 10.0 percent, 15.0 percent, and 25.0 percent for verification purposes.

XRF Tests

For benchtop XRF test, binder specimens were first inserted into stainless steel holders such that the surface with polypropylene film was at the bottom. Then they were together placed on an enclosed turret, which could hold 12 samples at a time. The instrument automatically moves these specimens in and out of an enclosed test chamber during the tests. For handheld XRF test, binder specimens were inserted into a specialized sample holder such that the surface with polypropylene film was at the top. The handheld XRF instrument itself was brought in contact with the film for the test.

Elements of interest were selected based on an inter-lab repeatability study conducted in collaboration with TxDOT. Eight sets of calibration standards were first prepared by the Texas A&M Transportation Institute (TTI) and then tested using a high power benchtop WDXRF unit at TxDOT, a medium power benchtop WDXRF unit at TTI, and a low-power handheld EDXRF at TTI to determine common elements that would be detected by all of these instruments. Because there was difference in the capacity of these instruments, the numbers of times for any given element detected using one instrument, as expected, was completely different from those detected with the other instrument. However, this inter- and intra-lab study revealed that a close correlation exists between the REOB dosages and XRF readings obtained from a given instrument. This study also revealed that each of these instruments could detect elements that are commonly present in asphalt binders, REOB, and PPAs as reported in previous studies (Arnold and Nelson 2015; Arnold and Shastry 2015; Barborak et al. 2016; D'Angelo et al. 2012; Hesp and Shurvell 2010; Wielinski et al. 2015). Therefore, it was decided that the REOB/PPA/GTR detection methods should be developed using elements that could be always detected by these instruments. A total of 11 such elements were found to satisfy this criterion and were therefore selected as the elements of interest in XRF testing. Table 4 lists these elements with their chemical symbols.

Table 4. Elements and Their Chemical Symbols.

Element	Chemical Symbol
Calcium	Ca
Phosphorous	P
Copper	Cu
Molybdenum	Mo
Zinc	Zn
Potassium	K
Sulfur	S
Vanadium	V
Iron	Fe
Nickel	Ni
Silicon	Si

XRF Test Results and Discussion

Table 5 presents the identified elements and associated intensities obtained from the benchtop XRF tests on selected base binders and REOB samples alone. The table clearly demonstrates that the intensities of the selected elements in the base binders are drastically different than those of the corresponding elements in REOB. For example, the intensity of Zn ranged from 0 kcps to 1.47 kcps in binders, while it ranged from 10.82 to 22.81 kcps in REOB. The fact that the intensities of Ca, P, K, Mo, Cu, and Zn were very low in binders but quite significant in REOB signifies that the presence or absence of one or more of these elements can be used to confirm or deny the presence of REOB in binders. The table also demonstrates that both base binders and REOB vary from one source to another, potentially resulting in different properties despite the use of the same binder-to-REOB dosage ratio. FHWA researchers proposed a flowchart as shown in Figure 14 to determine whether or not REOB and GTR exist in asphalt binders (Arnold 2014). Basically, a binder does not contain any REOB under the following three conditions:

- If binder tests negative for Zn (e.g., D6422 binder).
- If binder tests positive for Zn, but negative for Cu and Mo (e.g., C6422, E6422, G6422).
- If binder tests positive for Zn and Mo but negative for Cu (e.g., B6422 binder: 0.77 kcps is too low to confirm there is REOB).

Based on this analysis, Table 5 shows that none of the selected binders contained any REOB.

Table 5. XRF Measurement of Element Intensity in Selected Base Binders and REOB.

Measured Intensity of Elements (kcps)												
Material	Source	Ca	K	P	Mo	Cu	Zn	S	Ni	Fe	V	Si
Binders	B6422	-	0.15	0.04	0.77	-	0.76	80.85	0.70	-	0.18	0.03
	C6422	-	0.16	-	-	-	1.47	82.38	0.71	0.08	0.21	-
	D6422	-	0.14	0.30	-	-	-	82.08	0.30	0.19	0.08	-
	E6422	0.06	0.21	-	-	-	0.44	66.94	0.77	0.21	0.23	-
	G6422	0.03	0.15	0.02	-	-	1.24	89.64	0.64	0.06	0.67	-
REOB	R1	27.57	1.78	5.23	14.33	2.29	18.96	65.74	-	5.00	-	-
	R2	22.29	5.93	3.17	11.50	1.33	15.66	42.19	-	2.24	-	-
	R3	31.25	1.53	5.43	14.75	1.90	22.81	58.78	0.29	6.24	-	-
	R4	14.97	0.97	2.45	7.00	0.86	10.82	25.40	-	1.54	-	-
	R5	19.85	0.83	3.14	11.29	1.17	15.02	48.14	-	1.60	-	-
	R6	22.36	-	3.82	10.32	1.94	16.53	53.76	-	3.35	-	0.15

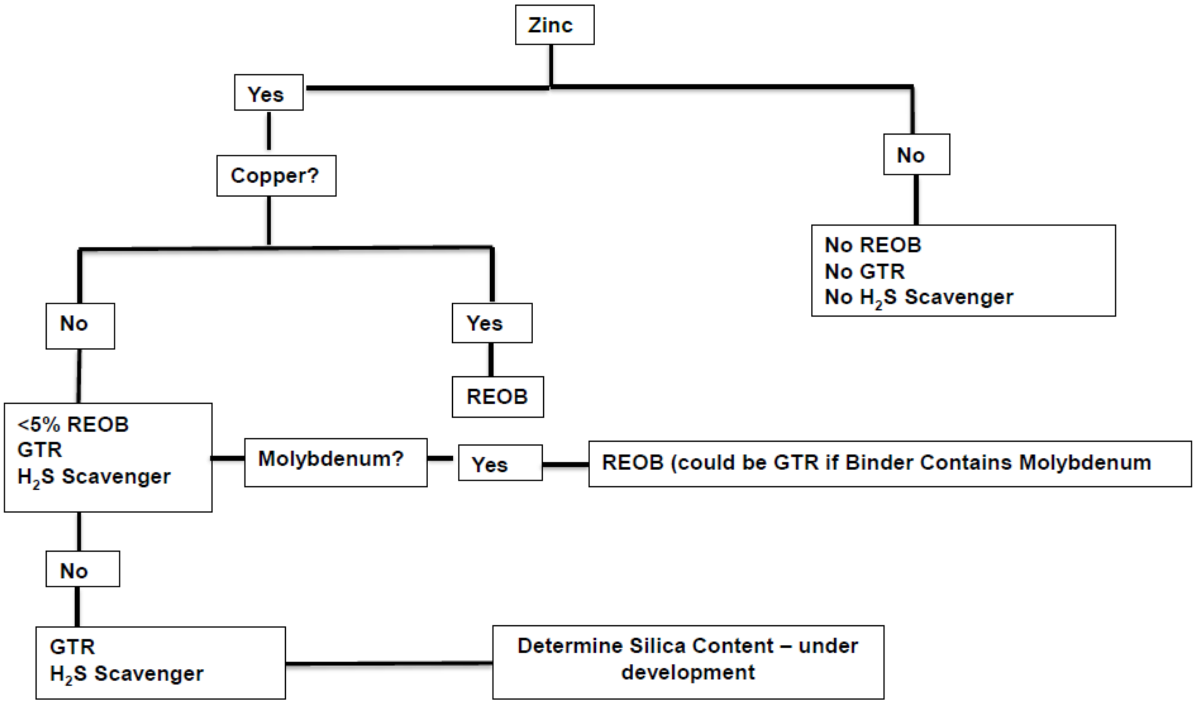


Figure 14. Flowchart to Determine REOB/GTR/H_2S Scavenger (Arnold 2014).

Table 6 presents benchtop XRF readings of element intensities (kcps) in 16 out of 414 asphalt binder/REOB blends. Similarly, Table 7 presents handheld XRF readings of element concentrations (ppm) in these specimens. The tables clearly show that, for a known binder source and known binder PG and known REOB content, the intensity of any given element varies from one source of binder to another (see rows for S#1 to S#4 in Table 6 and Table 7). The tables also show that, for a known source of binder and known source and content of REOB, the intensity of any given element can change from one PG to another grade (e.g., see rows for S#4 to S#7). Likewise, the same tables also display that the intensity of elements vary when source of REOB changes but the source and PG level of asphalt binder and the REOB content remain the same (see rows for S#7 to S#12). Furthermore, the tables also demonstrate that there is a significant change in element intensity when REOB content reduces from 20 percent to 0 percent (i.e., virgin binders without any REOB), while the source and PG level of the binder and the source of REOB remain the same (see rows for S#12 to S#16). Table 6 and Table 7 also indicate that some elements that test positive, mainly potassium (K), in benchtop XRF tests may test negative in handheld instrument tests. To synopsize, element intensity changes is impacted by four factors: (1) binder source, (2) binder PG, (3) REOB source, and (4) REOB content. Therefore, the key to accurate estimation of REOB content is to develop a method of considering all these four factors.

Table 6. Element Intensities Measured Using Benchtop XRF Instrument.

Sample	Binder		REOB		Measured Intensities of Element (kcps)										
	Source	PG	Source	%	Ca	K	P	Mo	Cu	Zn	S	Ni	Fe	V	Si
S#1	B	64-22	R1	20	5.39	0.48	1.17	4.1	0.63	17.6	55.1	0.41	1.78	0.08	0.06
S#2	D	64-22	R1	20	4.82	0.4	1.31	3.6	0.49	15.1	67.1	0.3	1.07	0.08	0.04
S#3	E	64-22	R1	20	5.38	0.44	1.14	4.2	0.62	17	55.7	0.51	1.14	0.16	0.05
S#4	G	64-22	R1	20	5.64	0.49	1.34	4.4	0.61	16.6	72.6	0.48	1.06	0.55	-
S#5	G	70-22	R1	20	4.55	0.38	1.06	3.9	0.56	14.4	72.9	0.49	0.91	0.46	0.08
S#6	G	70-28	R1	20	5.47	0.45	1.18	4.3	0.62	17.6	53.7	0.34	1.31	0.12	0.06
S#7	G	76-22	R1	20	7.13	0.6	1.72	4.4	0.74	18.7	65.6	0.58	1.35	0.51	-
S#8	G	76-22	R2	20	3.88	1.1	0.72	3.1	0.3	9.6	70.8	0.48	0.47	0.58	0.05
S#9	G	76-22	R3	20	5.81	0.39	1.18	4.2	0.46	15.2	71	0.57	1.33	0.58	0.12
S#10	G	76-22	R4	20	3.45	0.35	0.79	2.8	0.32	9	68.9	0.54	0.59	0.55	-
S#11	G	76-22	R5	20	3.28	0.24	0.68	2.7	0.23	10	70.6	0.55	0.35	0.59	0.04
S#12	G	76-22	R6	20	3.77	0.83	0.92	3.1	0.42	11.9	70.8	0.47	0.7	0.61	0.04
S#13	G	76-22	R6	10	1.86	0.46	0.45	1.6	0.25	6.5	77.2	0.54	0.37	0.66	0.04
S#14	G	76-22	R6	5	1.03	0.33	0.26	1	0.24	4	80.4	0.65	0.26	0.67	0.03
S#15	G	76-22	R6	2.5	0.47	0.17	0.11	0.7	-	2.3	82.3	0.68	0.13	0.69	-
S#16	G	76-22	R6	0	0.09	0.16	0.04	0.4	-	1.1	86.6	0.62	0.13	0.70	-

Table 7. Element Intensities Measured Using Handheld XRF Instrument.

Sample	Binder		REOB		Measured Concentrations of Element (parts per million or ppm)										
	Source	PG	Source	%	Ca	K	P	Mo	Cu	Zn	S	Fe	Ni	V	Si
S#1	B	64-22	R1	20	9441		1800	112	71	1880	113745	251		715	
S#2	D	64-22	R1	20	9867		2475	107	74	1965	110731	289		265	302
S#3	E	64-22	R1	20	11848		2285	118	80	2112	95621	325		605	
S#4	G	64-22	R1	20	10236		2174	111	75	2087	117876	281		1958	
S#5	G	70-22	R1	20	10510		2089	114	74	1949	128653	258		2126	
S#6	G	70-28	R1	20	12184		2346	115	93	2159	93714	362		460	
S#7	G	76-22	R1	20	11320		2428	109	77	2004	121632	260		2684	
S#8	G	76-22	R2	20	8946	2515	1485	89	34	1205	122712	86		2804	
S#9	G	76-22	R3	20	13423		2411	126	66	2067	124929	399		2818	
S#10	G	76-22	R4	20	7473		1434	67	36	1061	118628	113		2821	
S#11	G	76-22	R5	20	7354		1367	78	23	1262	121385	62		2883	
S#12	G	76-22	R6	20	8612	1479	1790	85	51	1531	123463	166		2845	
S#13	G	76-22	R6	10	4543	410	746	46	28	805	132906	61		3169	
S#14	G	76-22	R6	5	2372		393	22		496	136837			3375	
S#15	G	76-22	R6	2.5	1197		194	15		303	139478			3460	
S#16	G	76-22	R6	0	139			8		136	143203			3494	

DEVELOPMENT OF NEW DETECTION METHODS FOR REOB

Two different detection methods are developed in this study, one for the benchtop unit and the other for the handheld unit. Each one is described below.

Benchtop XRF-Based REOB Detection Method

Built on the work done by TxDOT (Barborak et al. 2016), this research team developed a three-step systematic method for quantifying REOB content in asphalt binders using the benchtop XRF unit: (1) identify binder sources and PG levels, (2) identify REOB sources and select a calibration standard, and (3) estimate REOB content.

Step 1: Identify Binder Sources and PG Levels

Researchers first plotted the S and V intensities of all blends belonging to 96 calibration standards prepared using 16 binders each with six REOB for this study, as seen in Figure 15(a). The figure clearly shows that asphalt binder/REOB blends conglomerated into two distinct clusters—one cluster containing blends that read a V intensity of 0.25 kcps or smaller, and the other region including blends that read a V intensity of 0.35 kcps or greater. The results actually showed that PG64-22 and PG70-22 binders from the binder source E and PG76-22 from binder sources E and F belonged to the group with 0.35 kcps or higher intensity in terms of V. Therefore, researchers concluded that V intensity of 0.30 kcps could be effectively used to discriminate the cluster that the unknown REOB belonged to, as illustrated in Figure 15(b). This particular figure also shows that blends of different grades of binders obtained from the same supplier may belong to two different clusters. For example, in this case, blends prepared with PG64-22, PG70-22, and PG76-22 binders belonged to the cluster with greater than 0.30 kcps V intensity, while the blends prepared with PG70-28 binders belonged to the cluster with smaller than 0.30 kcps V intensity.

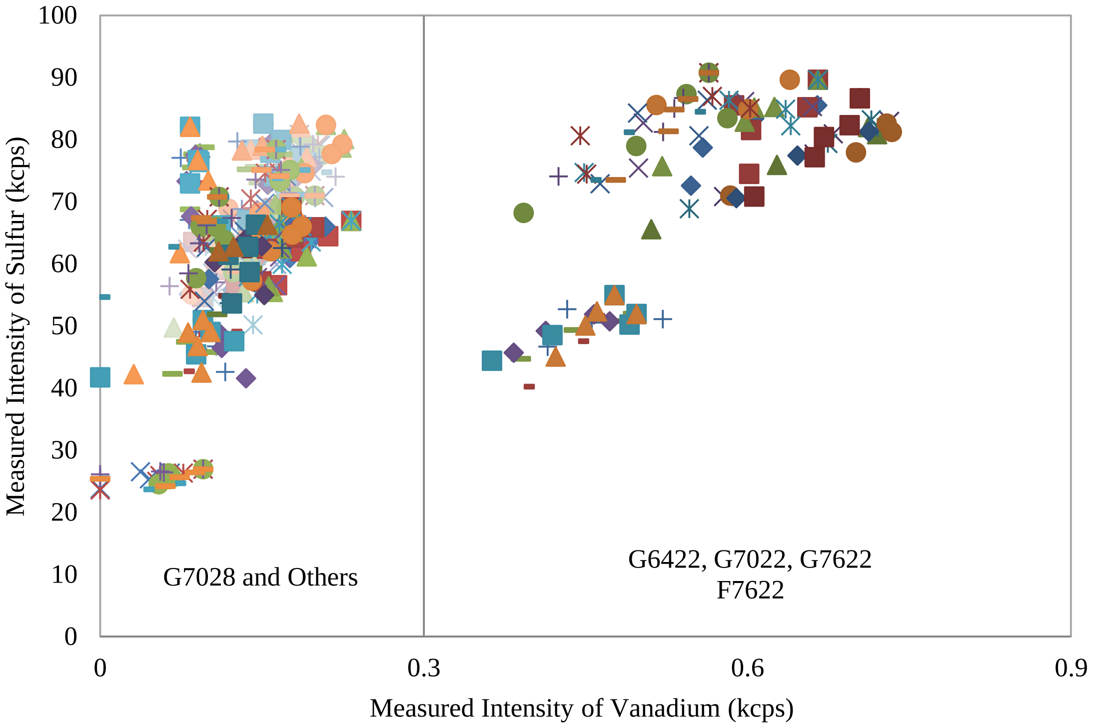
Next, a scientific method is needed to select calibration standards within each cluster. In this study, the closeness of the unknown sample to each of the 96 calibration standards was calculated in terms of cumulative sum of distance square (D^2) using the S vs. V plot to determine all possible calibration standards:

$$D_i{}^2 = \sum_{j=\text{REOB 1}}^{\text{until REOB 6}} \sum_{i=0\%}^{until\ 20\%} d_i{}^2 \tag{1}$$

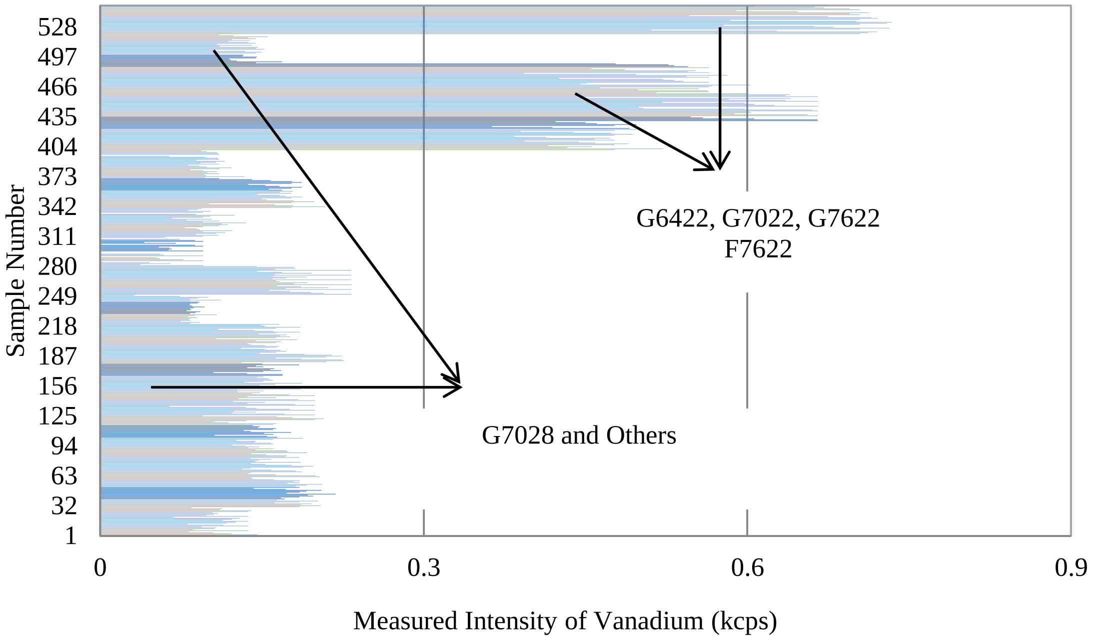
Where

$$d_i{}^2 = \left(nS_{unknown} - nS_{standard,i}\right)^2 + \left(nV_{unknown} - nV_{standard,i}\right)^2 \tag{2}$$

where, closeness parameter D^2 refers to the total square distance of the S vs. V of the unknown sample from all 30 S vs. V data points (i.e., 1 binder source × 1 binder PG level × 6 REOB sources × 5 REOB dosages). Similarly, d refers to the distance of the unknown sample from each of the 30 blends prepared using a given binder and six REOB at five dosage rates (see illustration in Figure 16).



(a) Measured intensity of S versus measured intensity of V



(b) Measured intensity of V

Figure 15. XRF Measurements of S and V in Binder/REOB Blends.

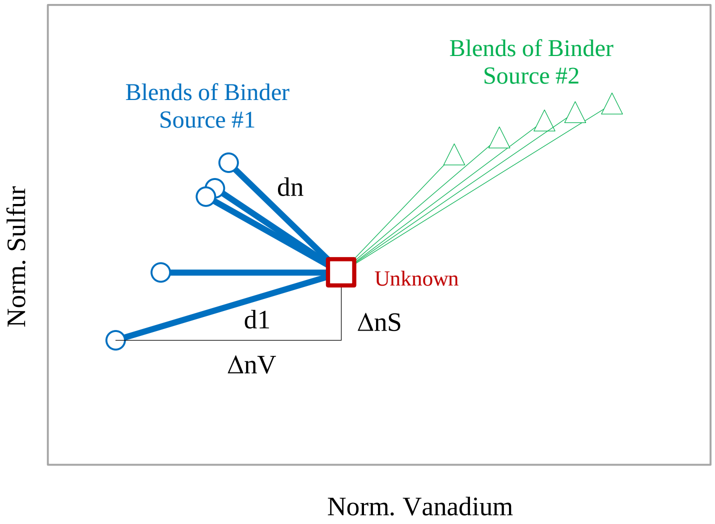


Figure 16. Illustration of Closeness of an Unknown Sample with Known Sets of Blends.

Since S intensity is significantly higher than V intensity, before this calculation, the intensities were first normalized with respect to the maximum intensities of corresponding elements obtained from each samples. Note that the normalization does not change the relative location of the measured data points, as illustrated in Figure 17. The normalized intensities of S and V are represented by variables nS and nV, respectively. The binder sources and the binder PG levels that are within 50 percent error margin of the least value of D^2 were selected as binders that were likely used with REOB to obtain the unknown sample.

For the purpose of illustration, a binder sample with unknown REOB source and content was chosen; the XRF test of this particular sample showed intensities of S, V, Ca, K, and Zn as 76.93 kcps, 0.16 kcps, 1.93 kcps, 0.27 kcps, and 6.6 kcps, respectively. The use of the analysis step described in the foregoing paragraph showed that the sample was closest to the calibration standard prepared with the C6422 binder, as illustrated in Figure 17.

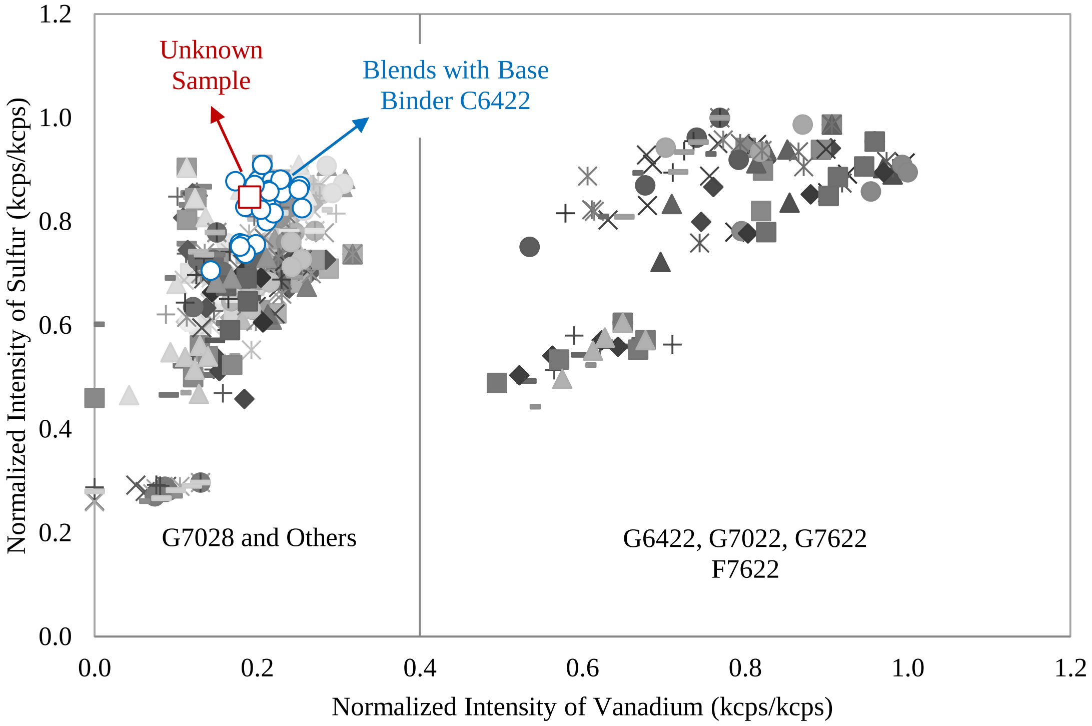
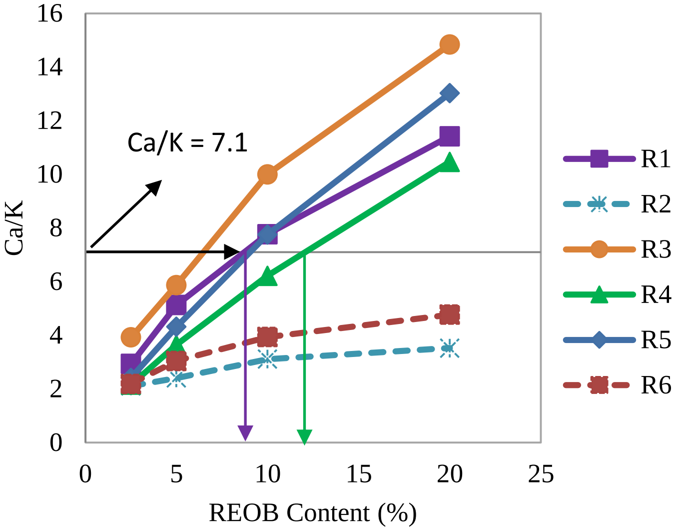


Figure 17. Normalized Intensities of S and V.

Step 2: Identify REOB Source and Calibration Standard

Once all possible binder sources and PG levels were identified, the Ca/K vs. REOB% curves obtained from calibration standards containing the REOB from six sources were then used to identify the possible REOB content based on each Ca/K ratio of the unknown sample. In this study, the Ca/K ratio was particularly used to identify the likely sources of REOB because the Ca/K values of blends prepared with REOB obtained from R1, R3, R4, or R5 were found quite different from the Ca/K values of blends prepared with REOB obtained from R2 or R6 at the same dosage rates. Figure 18 exemplifies a case wherein the Ca/K value of 7.1 kcps/kcps from an unknown sample was used to calculate the possible REOB content using all six calibration curves. As can be seen, calibration standards with REOB obtained from R2 or R6 showed very distinct trends compared to the other four standards, and consequently yielded very high REOB content, which is rarely used in asphalt modification. As such, the four standards with REOB obtained from R1, R3, R4, or R5 sources were determined to be candidate REOB sources for the unknown sample.

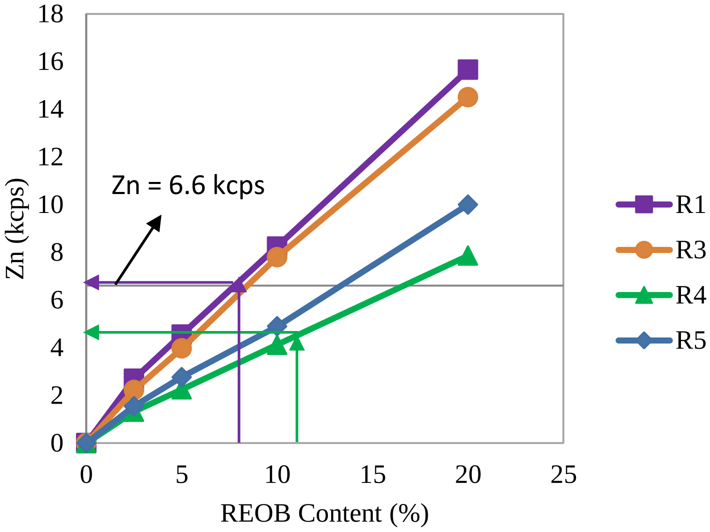
Thereafter, the REOB contents estimated as above were used to estimate the intensity of Zn in the unknown sample using calibration curves of Zn versus REOB% from each REOB source. The percent error between estimated and measured intensities of Zn for each REOB source was calculated. The main objective of this particular step was to determine the calibration standard that best estimates the Zn intensity.



REOB	Estimated REOB%
R1	8.1
R2	102.1
R3	5.8
R4	11.4
R5	8.7
R6	45.4

Figure 18. Estimation of REOB Content in an Unknown Sample Using Ca/K.

Figure 19 presents a case wherein calibration standards with REOB obtained from R1, R3, R4, and R5 estimate Zn intensity at a reasonable level of error; REOB obtained from R2 or R6, as expected, yielded very high error percentages. The standard with the minimum possible error of Zn intensity (R1 in this case) was finally selected as the REOB source of the unknown sample.



REOB	Estimated Intensity of Zn (kcps)	Error %
R1	6.7	5
R3	4.6	28
R4	4.7	27
R5	4.4	30

Figure 19. Estimation of Zn Intensity in an Unknown Sample Using Approx. REOB.

Step 3: Estimate REOB Content

Finally, the Zn calibration curve belonging to the standard with the identified REOB source was used to estimate REOB content in the unknown sample. In this particular case, the calibration standard with REOB from R1 source was selected, resulting in 7.5 percent effective REOB content, as illustrated in Figure 20.

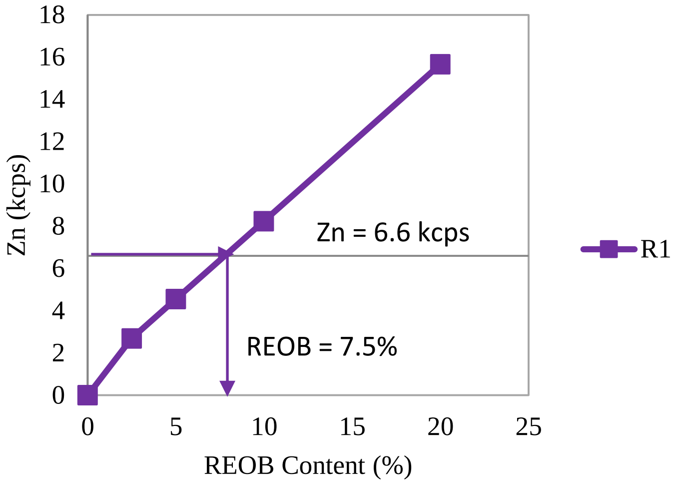


Figure 20. Estimation of REOB Content in an Unknown Sample Using Zn.

Handheld XRF-Based REOB Detection Method

As mentioned earlier, Table 6 and Table 7 showed that some elements that test positive, mainly K, in benchtop XRF tests may test negative in handheld instrument tests. Since K plays a key role in REOB detection using the benchtop XRF, it was deemed impossible to use the exact same method for the handheld XRF unit. After carefully reviewing all the measured XRF data, TTI researchers developed a two-step systematic method for quantifying REOB content in asphalt binders using a handheld XRF unit: (1) identify binder sources and PG levels, and (2) estimate REOB content.

Step 1: Identify Binder Sources and PG Levels

The first step of this method is to identify all possible sources and PG levels of binders using the measured concentration of S and V in exactly the same way as the benchtop method.

TTI researchers first plotted normalized concentrations of S and V in each specimen belonging to the 96 calibration standards prepared using 16 binders and 6 REOB at five different dosage rates (see Figure 21). As before, asphalt binder/REOB blends conglomerated into two distinct clusters before and after the normalized V concentration value of 0.4 ppm/ppm. The placement of binders in this figure is similar to the placement of binders shown in Figure 17, that is, G6422, G7022, G7622, and F7622 gathered above this value, while others gathered below this value.

Figure 21 also illustrates the position of an unknown sample with 82513.8 ppm of S and 2149.9 ppm of V (or normalized concentration of 0.55 ppm/ppm for S and 0.62 ppm/ppm for V) beyond the 0.4 ppm/ppm margin.

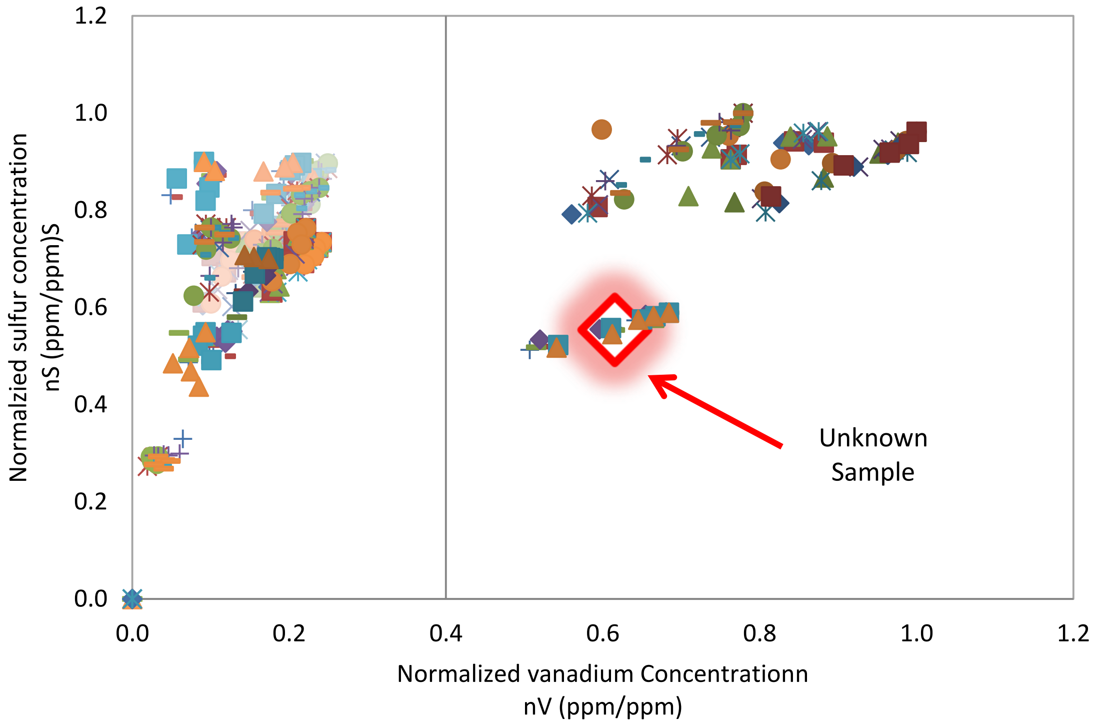


Figure 21. Normalized Concentrations of S and V.

Similarly, closeness of the unknown sample to each of the 96 sets of calibration standards was calculated in terms of cumulative sum of distance square (D^2) using Equations 1 and 2. The binder sources and PG levels that were within 50 percent error margin of the least D^2 value were selected as the binders that were most likely used to obtain the unknown sample. The use of the analysis step described in the foregoing paragraph showed that the unknown sample (see Figure 21) was closest to the calibration standard prepared with the F7622, as illustrated in Table 8.

Step 2: Estimate REOB Content

Handheld XRF detected only four out of six previously identified signature elements of REOB (they being Ca, Mo, Zn, and P, respectively) in each samples used in this study; K and Cu were not always detected (see Table 8 for illustration). However, P could be contributed by PPA as well, so it is not suitable for estimating REOB content. Therefore, only the three elements—Ca, Mo, and Zn—are useful for estimating REOB content in asphalt binders.

Figure 22 presents the calibration curves of Ca, Mo, and Zn (i.e., element concentrations versus REOB content) for a selected binder source and PG and the six REOB sources. Using these calibration curves, REOB contents that correspond to the measured concentration of a selected element in an unknown sample were estimated for each sources of REOB, resulting in a total of six different estimates of REOB contents for each element type. The six values of REOB contents estimated for each source of REOB were then averaged to calculate three different values of average REOB content, one for each element. The three values of REOB contents estimated using Ca, Mo, and Zn concentrations of the unknown sample and Ca, Mo, and Zn calibration curves of standards from the previously selected binder source were again averaged to estimate the final estimated value of REOB content in the unknown sample.

Table 8. Closeness of the Unknown Sample to Selected Standards.

Blend	Closeness from the Unknown Sample (D^2)
A6422	9.15
B6422	7.14
B6428	7.09
B7022	6.55
B7028	6.74
C6428	8.15
C7622	6.90
D6422	12.99
E6422	5.41
E7622	13.14
E-HP	8.29
F7622	0.13
G6422	4.91
G7022	4.98
G7028	6.59
G7622	6.90

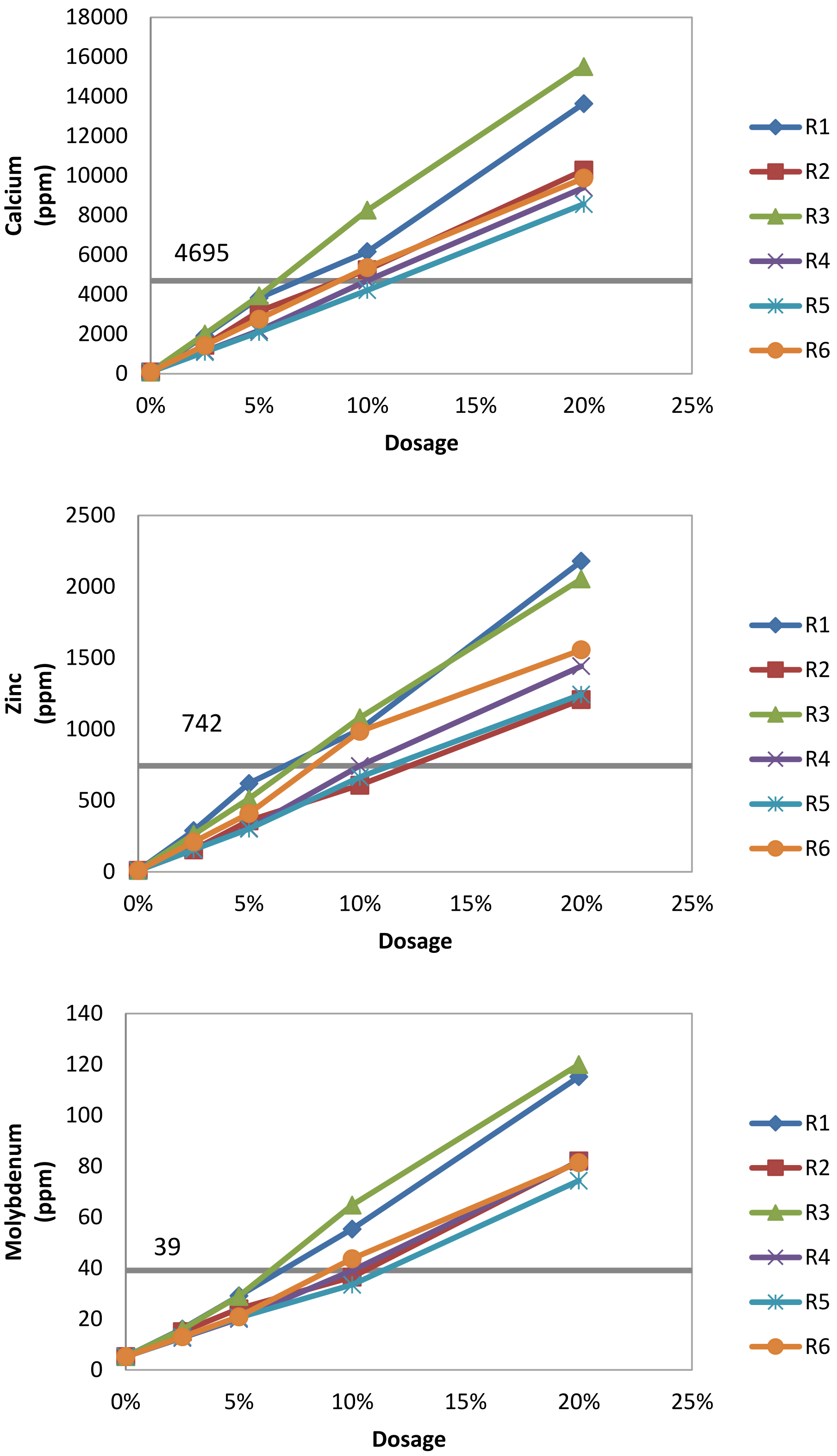


Figure 22. REOB Content in an Unknown Sample Using Ca, Zn, and Mo Concentrations.

Table 9 shows that the REOB content in the unknown sample illustrated in Figure 21 was estimated as 8.9 percent. This value was 11.3 percent off from the actual REOB content.

Table 9. REOB Content in an Unknown Sample Using Ca, Mo, and Zn Concentrations.

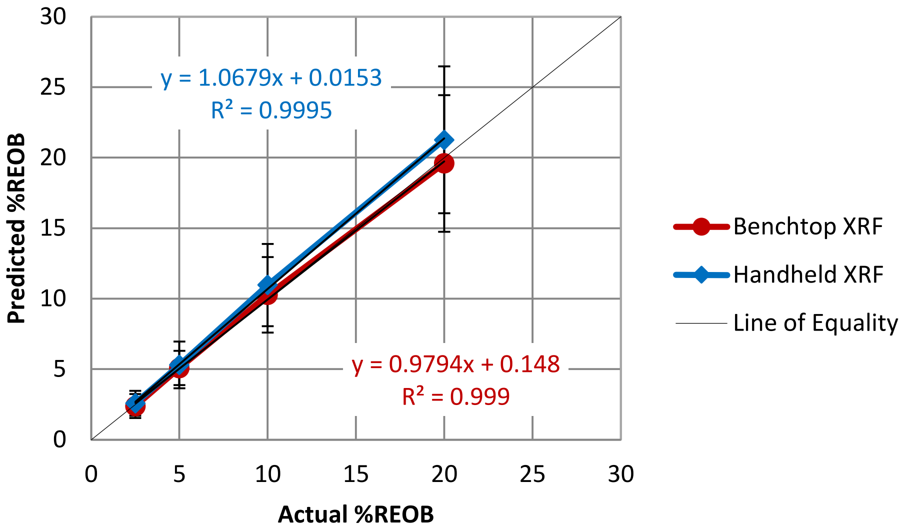
Binder	REOB	Estimated REOB% Using Calibration Curve			Average
		Ca	Mo	Zn	
F7622	R1	6.9	6.6	6.8	6.7
	R2	8.8	9.2	12.1	10.0
	R3	5.9	6.2	7.1	6.4
	R4	10.1	9.4	10.4	9.9
	R5	11.0	10.3	11.8	11.0
	R6	9.1	9.1	8.8	9.0
Average		8.6	8.5	9.5	8.9

VERIFICATION OF THE DEVELOPED REOB DETECTION METHODS

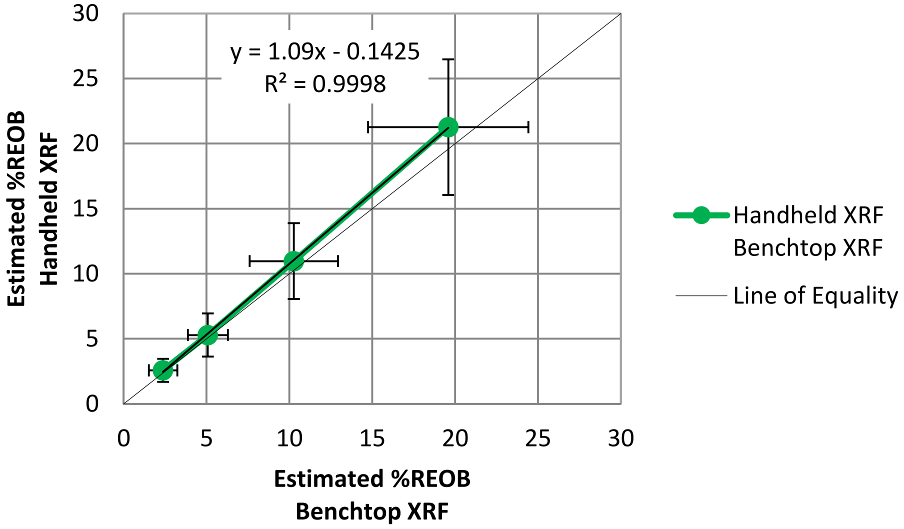
Verification with Known Calibration Samples

To verify the effectiveness of the developed methods in estimating REOB content in unknown sample, each of the 384 calibration samples were treated as unknown samples and encoded a random identification number to avoid bias. First of all, the accuracy of the handheld XRF based method is checked. The REOB contents in each of these binders were estimated using the two-step analytical procedure described in the foregoing sections. Figure 23(a) presents the average values of estimated vs. actual REOB contents in asphalt binder samples. Additionally, the estimated REOB contents from the benchtop XRF based method were calculated and are also shown in Figure 23(a). Figure 23(b) presents the comparison of average values of REOB contents between the benchtop XRF instrument and the handheld XRF unit (Karki and Zhou 2017). Compared to the handheld XRF based method, the benchtop XRF based method, as expected, had better accuracy. Meanwhile, the figure shows that the handheld XRF based method slightly overestimates REOB content. This slight overestimation can be attributed to the exclusion of the intermediate step of the benchtop XRF based method that is designed to determine REOB source before estimating their content. Nevertheless, the differences in REOB contents estimated using these two methods are not significant. The strong correlation between the actual REOB contents and the estimated values from both of these methods suggests that either one of these methods can used to adequately estimate the REOB content in any binder sample.

The standard deviations in Figure 23 suggest that there is some possibility of estimation error, which is expected because multiple sources of binders and REOB were used. Since state agencies are moving toward setting an upper limit for allowable REOB content way below 20 percent, this method is effective enough for the practical range of REOB use.



(a) Estimated vs. Actual %REOB



(b) Handheld vs. Benchtop XRF Results

Figure 23. Estimated versus Actual REOB Contents in Asphalt Binders.

Verification with Additional Unknown Samples

Twenty-four additional samples were specifically blended for the verification purpose. Note that these 24 samples were not used to develop the estimation method. These samples were prepared by mixing a new source of binder with 2.5, 5, 10, and 20 percent REOB from each of the six sources. Table 10 presents estimated REOB contents from the handheld XRF-based method. The table clearly demonstrates that the estimated REOB contents are within 20 percent estimation error in all 24 but 4 cases, resulting in over 80 percent success rate. The table further demonstrates that the handheld XRF based method can estimate the REOB content in asphalt binders within acceptable amount of error.

Table 10. Actual vs. Estimated REOB Content in Additional Verification Samples.

REOB	Estimated REOB%				Estimation Error%			
	2.5	5	10	20	2.5	5	10	20
R1	2.0	3.8	8.2	14.9	21	23	18	25
R2	2.7	4.9	9.9	18.5	7	3	1	8
R3	4.0	7.4	15.8	29.7	59	49	58	49
R4	2.3	4.5	9.8	17.2	8	10	2	14
R5	2.2	4.4	8.8	16.3	11	13	12	19
R6	2.9	5.8	10.4	23.7	18	16	4	18

DEVELOPMENT AND VERIFICATION OF PPA DETECTION METHOD

In addition to REOB, this research also developed a method to estimate PPA content. The detailed developing process is described below.

Selected Materials

Asphalt binder G5828 was blended with two different sources of PPA. TTI researchers used the following combination of materials to prepare calibration standards for detecting PPA levels in asphalt binders:

- Asphalt Binders:
  - 1 source—Source G.
  - 1 PG—PG 58-28 (denoted as G5828).
- PPA:
  - 2 sources—P1 and P2, respectively.
  - 5 dosage rates—0 percent, 0.25 percent, 0.50 percent, 1.0 percent, and 2.0 percent.

Selected Instruments

Both benchtop and handheld XRF instruments were used for this part of the study.

Sample Preparation

In total of nine samples, including G5828 binder and eight asphalt binder/PPA blends, were used for this part of the study. The blends were prepared by heating the binder in a conventional oven at its mixing temperature. Since PPAs are already in a liquid state at room temperature, they were directly added to the heated asphalt binder and then stirred with a spatula. The blends were reheated for five minutes and then stirred again with a spatula, three times in a row, to make them homogeneous. The samples were poured into double open-ended sample cups with a transparent polypropylene film on one side and opaque snap-on caps on the other side (see Figure 13). Similar to the REOB detection, two specimens were prepared for each sample, resulting in a total of 18 test specimens.

XRF Tests

Table 11 presents the measured intensities of elements present in the PPA-modified binders. The table shows that the selected binder, G5828, potentially contains some amount of REOB. With adding more PPA, the intensity of P increased and S decreased, while the intensity of the other elements remained unaffected. Since S is not related to PPA, only phosphorous readings were considered for further analysis.

Table 11. Measured Intensities of Elements in PPA-Modified Blends.

(a) Benchtop XRF Results

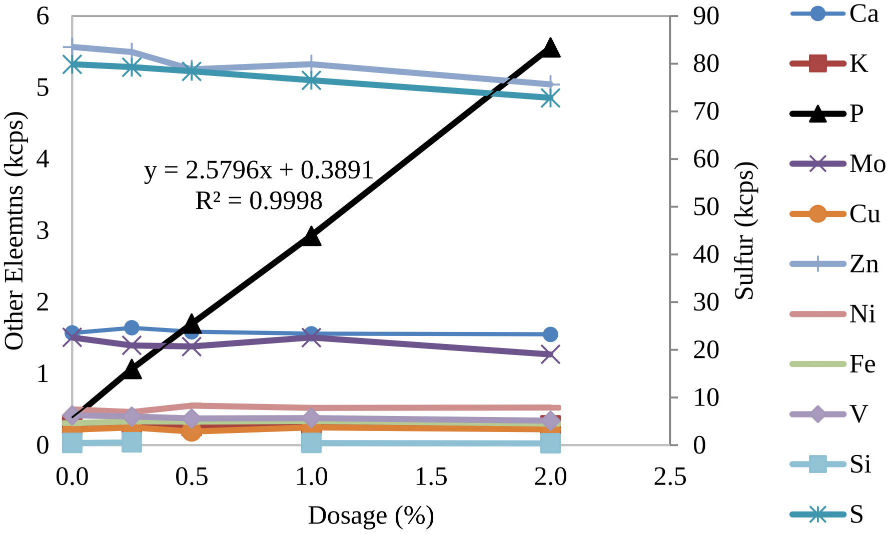
Binder	PPA		Measured Intensities (kcps)										
	Source	Dosage	Ca	K	P	Mo	Cu	Zn	S	Fe	Ni	V	Si
G5828	P1	0.00%	1.57	0.27	0.37	1.51	79.86	0.22	5.57	0.50	0.31	0.42	0.03
		0.25%	1.64	0.28	1.07	1.39	79.28	0.25	5.49	0.47	0.33	0.40	0.04
		0.50%	1.58	0.27	1.70	1.38	78.37	0.19	5.25	0.55	0.33	0.37	0.00
		1.00%	1.56	0.27	2.93	1.51	76.52	0.25	5.33	0.52	0.34	0.38	0.03
		2.00%	1.55	0.28	5.56	1.27	72.83	0.22	5.04	0.53	0.30	0.34	0.03
	P2	0.00%	1.57	0.27	0.37	1.51	79.86	0.22	5.57	0.50	0.31	0.42	0.03
		0.25%	1.62	0.27	0.95	1.29	78.30	0.21	5.57	0.48	0.30	0.41	0.04
		0.50%	1.62	0.27	1.53	1.54	77.04	0.25	5.27	0.45	0.34	0.40	0.02
		1.00%	1.55	0.26	3.25	1.44	74.69	0.25	5.29	0.58	0.27	0.39	0.00
		2.00%	1.51	0.25	4.97	1.47	73.13	0.00	5.13	0.50	0.29	0.42	0.00

(b) Handheld XRF Results

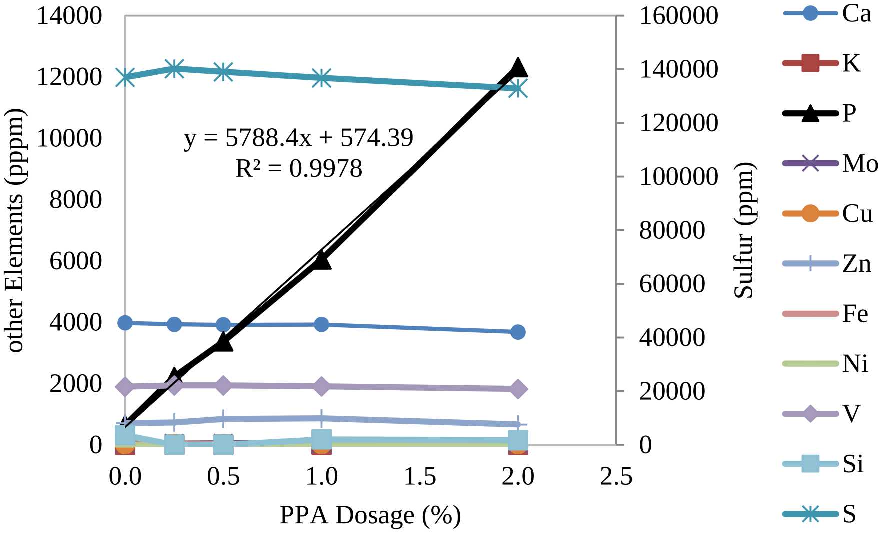
Binder	PPA		Measured Concentrations (ppm)										
	Source	Dosage	Ca	K	P	Mo	Cu	Zn	S	Fe	Ni	V	Si
G5828	P1	0.00%	3973	0	639	39	136988	20	704	10	0	1891	313
		0.25%	3929	0	2217	40	140193	27	728	35	0	1936	0
		0.50%	3913	0	3370	44	139011	11	846	29	0	1936	0
		1.00%	3924	0	6040	38	136735	24	863	20	0	1901	178
		2.00%	3677	0	12313	43	132825	27	659	49	0	1819	151
	P2	0.00%	3973	0	639	39	136988	20	704	10	0	1891	313
		0.25%	3934	0	1879	40	137845	12	718	57	0	1920	363
		0.50%	3791	0	3358	42	138685	30	703	21	0	1941	0
		1.00%	3698	0	7143	37	134856	24	693	21	0	1843	108
		2.00%	3859	0	10253	37	130588	25	652	21	0	1769	602

Development of PPA Estimation Method

Figure 24 presents the calibration curves of the Ca to Si elements in P1 blends obtained from the benchtop and handheld XRF tests. The curves clearly show that there is a linear relationship between the intensity of P and PPA content; however, other elements do not show such distinct relationships. This observation implies that PPA contributes to the change of the P intensity as expected because PPA is a compound of P. A very similar relationship between element P intensity with PPA content was found in P2 blends as well.



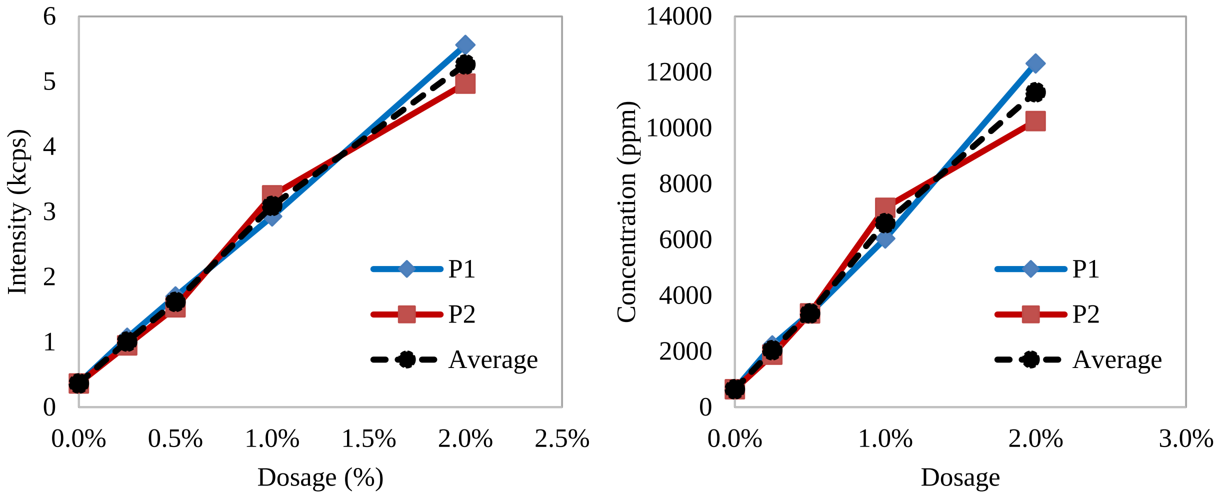
(a) Benchtop XRF



(b) Handheld XRF

Figure 24. XRF Measurements of Elements in the PPA-Treated Blends.

Figure 25 presents the calibration curves of P obtained from the two sets of PPA blends. The relationship between PPA content and average P content (concentration or intensity) shown in this figure was used to estimate PPA content in the binders.



(a) Benchtop XRF **(b) Handheld XRF**

Figure 25. Calibration Curve of P for the PPA-Treated Blends.

Verification of the PPA Estimation Method

Table 12 presents the estimated versus actual PPA content in modified binders. The table clearly shows that PPA can be estimated with reasonable accuracy using either the benchtop or the handheld XRF methods.

Table 12. Estimation of PPA in Modified Binders Using XRF.

Binder	**PPA**		**Estimated %PPA**	
	Source	Dosage	Benchtop	Handheld
G5828	P1	0.00%	0.00%	0.00%
		0.25%	0.26%	0.27%
		0.50%	0.52%	0.49%
		1.00%	1.02%	0.98%
		2.00%	2.08%	2.15%
	P2	0.00%	0.00%	0.00%
		0.25%	0.22%	0.21%
		0.50%	0.45%	0.48%
		1.00%	1.15%	1.19%
		2.00%	1.84%	1.77%

SUMMARY

This chapter described two methods for quantifying REOB/PPA content in asphalt binders: one using a three-step benchtop WDXRF spectroscopy technique and a two-step handheld EDXRF spectroscopy technique. Based on the data presented, the following observations were made:

1. The intensities or concentrations of Ca, Cu, K, Mo, P, and Zn in base binders are drastically different from the intensities of these elements in REOB/PPA.
2. Higher than normal intensity or concentration of Ca, Cu, K, Mo, Zn, and P elements in asphalt binders can be attributed to modification of binders with REOB. The intensities or concentrations of these elements are affected by REOB source, REOB content, binder source, and binder grade.
3. V intensity or concentration can differentiate binders into separate clusters. Blends prepared with asphalt binders with different PGs from the same supplier can belong to two different clusters.
4. Identification of more representative calibration standard is the key to more precise estimation of REOB content. The identification can be done by determining the calibration standard that is closest to the sample with unknown REOB content in normalized S versus V intensity or concentration plot. Both handheld and benchtop XRF methods include this essential step.
5. Closeness can be defined in terms of sum of the square of distance of an unknown sample from a given binder/REOB calibration set. A closeness parameter D^2 is good estimator of this closeness.
6. The calibration curves of the Ca/K intensity ratios and the calibration curves of Zn intensity versus REOB content can be used to identify potential sources of REOB and estimate the average value of REOB content in an unknown binder using a benchtop instrument method.
7. The calibration curves of Ca, Mo, and Zn concentrations versus REOB content can be used together to estimate the average value of REOB content in an unknown binder using a handheld instrument method.
8. The calibration curve of P intensity or concentration versus PPA content can be directly used to estimate the average value of PPA content in an unknown sample. This estimation can be done with both the handheld and benchtop methods; the accuracy level is quite similar. PPA content estimation does not depend on the source of PPA unlike REOB because PPA is a chemical compound but REOB are mixtures of known and unknown chemical compounds.
9. REOB/PPA contents estimated from both the handheld and the benchtop methods are close to the actual REOB contents and to each other. Both methods can predict the REOB content in asphalt binders without the beforehand knowledge of binder source, binder PG level, and REOB source.
10. As such, either of these two methods can be used to estimate the REOB/PPA content in an unknown sample. However, portable instrument-based REOB estimation method is a more practical option for quality control of binders than the benchtop instrument-based REOB estimation method because the portable instruments are much cheaper than benchtop instruments and can be transported easily to the field.

CHAPTER 4: REOB DETECTION METHODS FOR SEAL COAT BINDERS

INTRODUCTION

REOB is not only used in the asphalt binders, but it also is blended into seal coat binders. In Chapter 3, two XRF based REOB detection methods were developed and verified for asphalt binders. However, these two methods cannot be directly used for seal coat binders, because seal coat binders are often produced with GTR, and GTR has strong influence on XRF measurements. Thus, it is necessary to develop new REOB detection methods for seal coat binders.

In general, there can be four different cases for seal coat binder modification:

- Case I: No modification at all.
- Case II: Modified with GTRs only.
- Case II: Modified with REOB only.
- Case IV: Modified with REOB and GTRs together.

It is difficult to quantify the percentage of individual modifiers because both of these modifiers influence the concentrations of the same group of elements as shown in the following sections. To solve this problem, researchers developed a method that can determine their concentrations by differentiating their individual contributions to the concentrations of some key elements. Details are provided in the following sections.

SEAL COAT BINDER XRF TEST, RESULTS, AND ANALYSES

Selection of Materials

Researchers used the following combinations of materials to prepare calibration standards for detecting REOB and GTR in seal coat asphalt binders:

- Unmodified Seal Coat Binder:
  - AC10.
- GTR-Modified Seal Coat Binder:
  - AC10-2TR: AC10 (two sources) + 2%GTR.
  - AC10-5TR: AC10 + 5%GTR.
  - AC10-10TR: AC10 + 10%GTR.
  - AC20-5TR: AC20 + 5%GTR.
- Polymer-Modified Seal Coat Binder:
  - AC20-XP: AC20 + 5 percent Polymer.
- REOB:
  - 6 sources—R1 to R6.
  - 5 dosages—0 percent, 5 percent, 10 percent, 20 percent, and 30 percent.

XRF Instruments

Both benchtop and handheld XRF instruments previously described in Chapter 3 were used for this part of the study.

Sample Preparation

The GTR- and polymer-modified seal cost binders were directly obtained from seal coat binder suppliers. REOB-modification of these binders was carried out in TTI's McNew lab. In total, more than 400 calibration specimens were prepared by blending the six grades of seal coat binders (one unmodified, four GTR-modified, and one polymer modified) with the same six REOB as used in Chapter 3 at five different dosage rates and separating them into two replicates. The blends were prepared and separated into plastic cups following the same procedure as described in the previous chapter (see Figure 13).

XRF Test Results and Discussion

Table 13 presents the benchtop XRF readings of two seal coat binders, six REOB, one GTR, and one polymer. Note that this particular polymer is used to bond GTR with binder molecules. The key inferences from this table related to elements previously recommended for detecting REOB (Arnold and Shastry 2015; Barborak et al. 2016; Karki and Zhou 2017) and GTRs (Arnold 2014) in asphalt binders are as follows:

- Ca was always present in REOB and seal coat binders but not in the selected GTR and the polymer. Thus, Ca might be useful to differentiate the binders blended with GTR from the binders not blended with GTR.
- K was present in all binders and modifiers except the polymer and one REOB. However, the previous chapter showed that K might not be detected by handheld XRF unit due to its low intensity in some blends, and as such cannot help in determining the individual content of any modifier.
- P was present in both REOB and GTR. However, it is a signature element of PPA. Therefore, it was not used in this part of the study.
- Mo was always present in REOB but not in GTR, indicating Mo can be solely used to differentiate the binders that contain REOB from the binders that do not contain REOB.
- Cu was always absent in seal coat binders but present in modifiers except the polymer, but its low content, even in these modifiers, implies that the blends will have even less concentrations of element Cu. Thus, Cu cannot be used for the above mentioned objective.
- Zn was present in minimal amount in seal coat binders, moderate amount in REOB, but significant amount in GTR, implying the contribution of each of these materials to Zn concentration/intensity needs to be separated to determine their individual percentage.
- S and V were always present in seal coat binders, implying the S and V plot can be potentially used to identify source of binder as before.
- Silicon (Si) was present more significantly in GTR than in seal coat binders, polymer, and REOB. However, their intensities and corresponding concentrations in REOB-modified blends were quite small, as shown in Table 14 and Table 15. Therefore, it was

not used to estimate GTR in this study although a previous study suggested otherwise (Arnold 2014).

Table 13. Measured Intensity of Key Elements in Seal Coat Binders and Modifiers.

Measured Intensity of Elements (kcps)												
Material	Source	Ca	K	P	Mo	Cu	Zn	S	Ni	Fe	V	Si
Seal Coat Binders	#1	0.12	0.17	0.04	0.27	-	0.78	53.53	0.39	0.71	0.09	0.01
	#2	0.08	0.18	-	-	-	0.80	60.95	0.58	0.24	0.16	0.01
	#3	-	0.15	-	-	-	1.26	79.45	0.67	0.12	0.18	-
REOB	R1	27.57	1.78	5.23	14.33	2.29	18.96	65.74	-	5.00	-	-
	R2	22.29	5.93	3.17	11.50	1.33	15.66	42.19	-	2.24	-	-
	R3	31.25	1.53	5.43	14.75	1.90	22.81	58.78	0.29	6.24	-	-
	R4	14.97	0.97	2.45	7.00	0.86	10.82	25.40	-	1.54	-	-
	R5	19.85	0.83	3.14	11.29	1.17	15.02	48.14	-	1.60	-	-
	R6	22.36	-	3.82	10.32	1.94	16.53	53.76	-	3.35	-	0.15
GTR		3.32	0.62	0.12	-	2.43	170.40	18.94	-	-		2.19
Polymer		0.17	0.30	0.06	0.82	-	-	0.18	-	-	-	0.10

Table 14 and Table 15 present the benchtop and the handheld XRF readings of unmodified (row #1) and modified seal coat binders. The tables show that the intensity and concentration of each any given detected element increased with an increase in the percentage of GTR, REOB, or both; and that S displayed opposite trend as reported in previous chapters. In addition to intensities and concentrations of the selected 11 elements in these blends, the tables also show that the ratios of Zn/Ca have unique relationships with the increase in the percentage of modifiers. Table 14 shows that the ratio increases from 10.56 to 48.37 when GTR content increases from 0 percent to 10 percent, while it decreases from 10.56 to 3.01 in AC10 seal coat binder, and from 10.56 to 3.43 in AC10-5TR seal coat binder when REOB content increases from 0 percent to 30 percent. Table 15 indicates that this ratio increases from 0.30 to 2.44 when GTR content increases from 0 percent to 10 percent, while it decreases from 0.30 to 0.18 in AC10 seal coat binder, and from 0.30 to 0.21 in AC10-5TR seal coat binder when REOB content increases from 0 percent to 30 percent. These unique relationships suggest that the Zn/Ca ratio can be used to identify whether or not seal coat binders have been modified with GTR alone and then to determine the GTR content.

Table 14 and Table 15 also show that binders blended with GTR alone do not contain any Mo. Since Mo was contributed by REOB only, it was selected in this study to estimate the REOB content in a given binder that was modified with REOB alone or with REOB and GTR together. The calibration curve of Mo belonging to a source binder was used for this purpose. Similar to previous work, the normalized S vs. V (nS vs. nV) plot of seal coat binders and the analysis of closeness parameter were used to select binder source.

The estimated REOB content was further used to determine intensity or concentration of Zn contributed by REOB. If this estimated value is smaller than the measured intensity or concentration of Zn, it can be hypothesized that binder must have been modified with REOB and GTR together. In such cases, the difference in measured and estimated intensities or concentrations of Zn was used to determine the percentage of GTR in the binder using the Zn-calibration curve of the source binder.

Table 14. Measured Intensity of Key Elements in Seal Coat Binders.

Binder	GTR	REOB		Measured Intensity (kcps)											$\frac{Zn}{Ca}$
				Ca	K	P	Mo	Cu	Zn	S	Ni	Fe	V	Si	
AC10	0%	None	0%	0.08	0.18				0.80	60.95	0.58	0.24	0.16	0.01	10.56
	2%			0.13	0.17				3.81	60.31	0.53	0.30	0.15	0.07	28.55
	5%			0.19	0.21				8.41	56.90	0.57	0.43	0.15	0.16	44.75
	10%			0.33	0.20				15.94	55.13	0.44	0.60	0.13	0.33	48.37
	0%	R1	5%	1.37	0.24	0.30	1.17	0.02	5.26	59.10	0.56	0.46	0.18	0.02	3.85
			10%	3.38	0.36	0.77	2.71	0.42	11.47	55.19	0.52	0.86	0.14	0.04	3.39
			20%	5.61	0.49	1.23	4.06	0.61	17.75	50.91	0.44	1.20	0.13	0.04	3.16
			30%	8.88	0.64	1.88	6.51	0.94	26.71	46.14	0.45	1.67	0.11	0.05	3.01
	5%		5%	1.54	0.25	0.28	1.32	0.24	12.18	55.43	0.53	0.71	0.16	0.17	7.92
			10%	2.87	0.33	0.62	2.17	0.36	15.89	53.12	0.49	0.91	0.13	0.15	5.54
			20%	5.55	0.45	1.13	4.22	0.60	23.40	48.95	0.46	1.38	0.10	0.16	4.22
			30%	9.18	0.67	1.85	6.38	0.91	31.50	43.14	0.33	1.79	0.11	0.16	3.43

Table 15. Measured Concentration of Key Elements in Seal Coat Binders.

Binder	GTR	REOB		Measured Concentration (ppm)											$\frac{Zn}{Ca}$
				Ca	K	P	Mo	S	Cu	Zn	Ni	Fe	V	Si	
AC10	0%	None	0%	307			9	102287		93			798	163	0.30
	2%			422			9	100861		413			750	329	0.98
	5%			468			9	98579		1017	64		674	379	2.17
	10%			747			7	95005		1825	125		554	779	2.44
	0%	R1	5%	3281		553	28	99014	20	600	85		703		0.18
			10%	7824		1420	69	94187	45	1384	208		641	13	0.18
			20%	12540	294	2455	117	88368	89	2260	320		560	108	0.18
			30%	19845	877	3702	159	79880	139	3592	561		439	322	0.18
	5%		5%	3494		588	27	95018	21	1436	146		589	406	0.41
			10%	6657		1218	50	92837	42	1951	234		575	365	0.29
			20%	12650	317	2343	115	87106	96	2978	418		500	424	0.24
			30%	19844	1014	3863	137	77293	146	4098	594		392	470	0.21

DEVELOPMENT OF REOB DETECTION METHODS FOR SEAL COAT BINDERS

Based on the discussion of the XRF test results, researchers developed a flow chart for quantifying REOB content in seal coat binders, as shown in Figure 26. Depending on whether or not GTR exists, it is a four-step process. Detailed steps are described below.

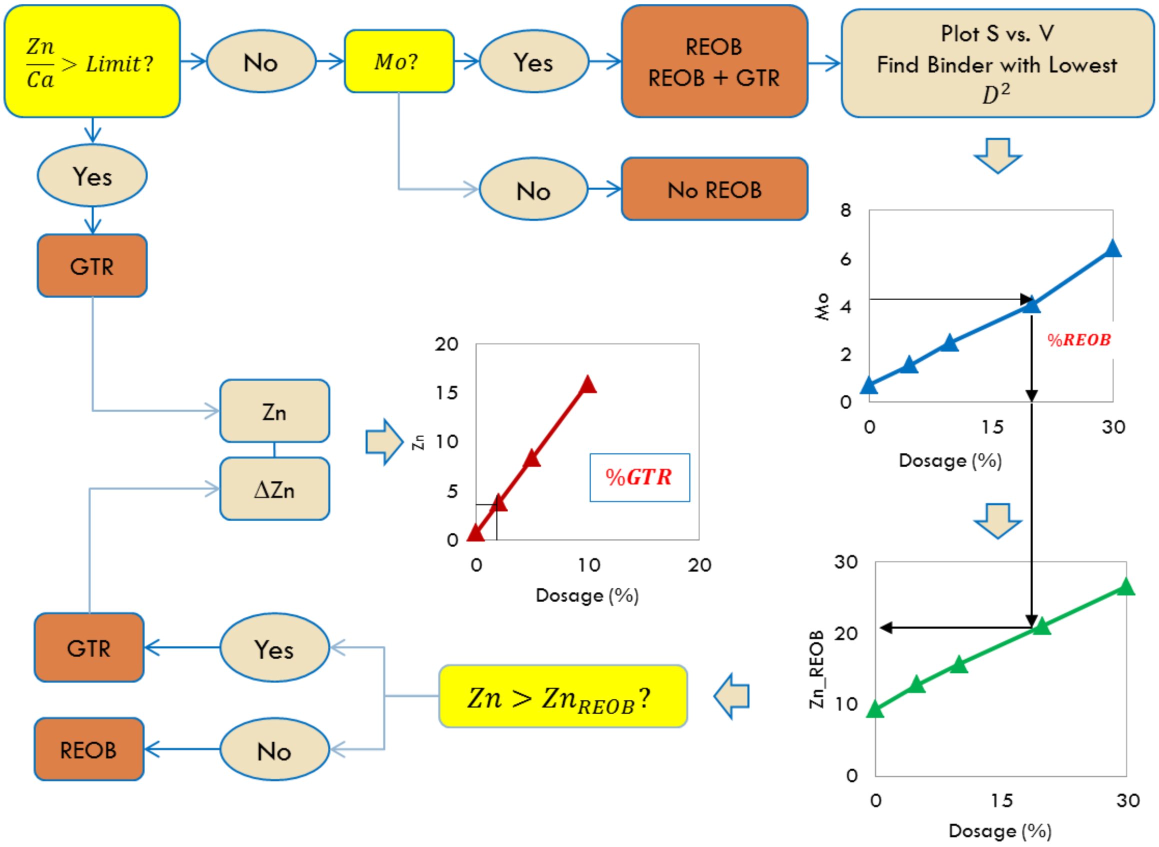


Figure 26. Flowchart to Determine REOB/GTR Content in Seal Coat Binders.

Step 1: Determine the Type of Modification Based on Zn/Ca Ratio

- GTR is present alone if:

$$\frac{Zn}{Ca} > \left(\frac{Zn}{Ca}\right)_{base\ binder}$$

In such case, GTR content is calculated using Zn vs. %GTR calibration curve of GTR-only modified binder.

- REOB is present alone or with REOB if:

$$\frac{Zn}{Ca} \leq \left(\frac{Zn}{Ca}\right)_{base\ binder}$$

For example, Zn/Ca values 4.23 and 0.23 were obtained for an unknown sample respectively from the benchtop and the handheld XRF analyses. Similarly, Zn/Ca values 10.56 and 0.30 were obtained for the base binder, respectively, from the benchtop and the handheld XRF analyses. Since this binder had less Zn/Ca values than the base binder (see Figure 27), it was concluded that it was not modified with GTR alone.

- The binder is not modified with REOB if:

$$Mo \leq Mo_{base\ binder}$$

- The binder is modified with REOB with or without GTR if:

$$Mo > Mo_{base\ binder}$$

For example, since selected binder contained 4.34 kcps (or 119 ppm) of Mo, that is more than base binders, researchers concluded that the binder was possibly blended with both REOB and GTR.

Table 16 Measured Elements.

XRF Instrument	Ca	Zn	Mo	S	V	Zn/Ca
Benchtop (kcps)	5.82	24.64	4.34	46.85	0.13	4.23
Handheld (ppm)	13323	3078	119	81485	511	0.23

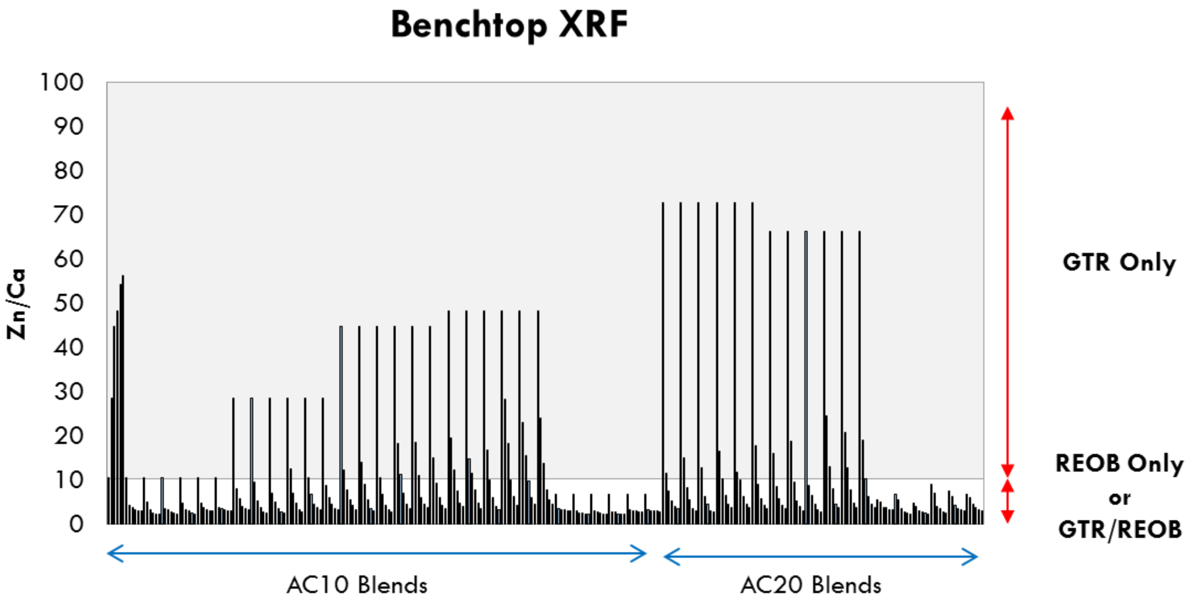


Figure 27. Zn/Ca Values of Seal Coat Blends.

Step 2: Determine Possible Sources of Binder Using S vs. V Plot

- Plot normalized S vs. V of all seal coat binders with known and unknown GTR and REOB contents (see Figure 28).
- Calculate D^2 closeness parameter for a given binder modified with all six REOB sources at all five dosages.
- Select binders with lowest D^2 value within a certain margin lowest D^2 value (herein, 40 percent) as source binder(s).

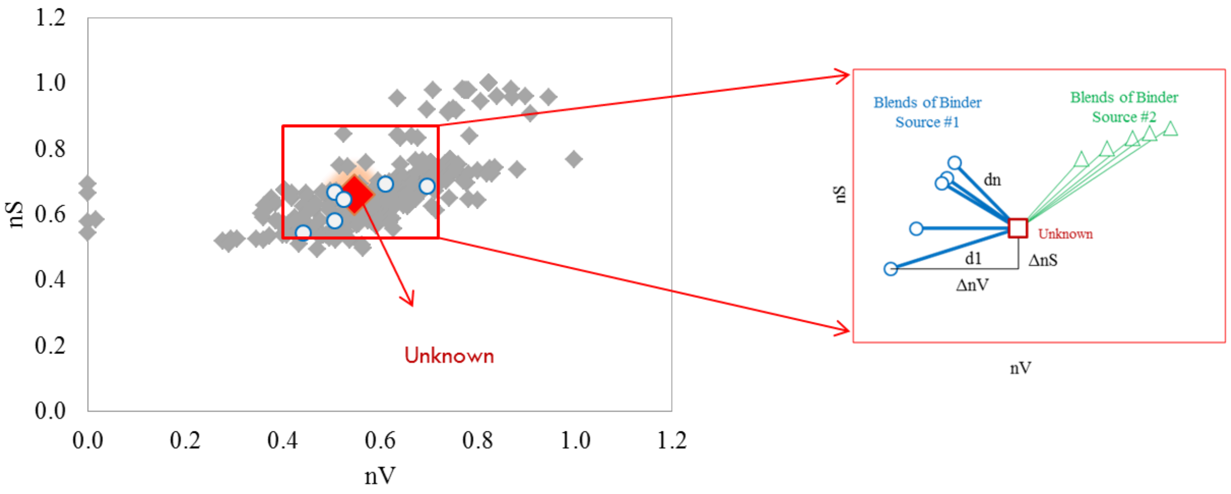
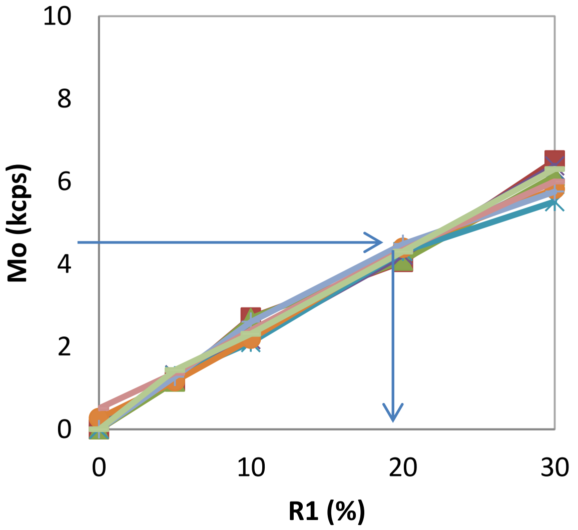


Figure 28. Normalized S vs. V Plot for Seal Coat Blends.

Step 3: Estimate REOB Content Using Mo Calibration Curve of Source Binder

- Estimate REOB content using measured Mo intensity or concentration and Mo vs. %REOB calibration curve of source binder (see Figure 29).

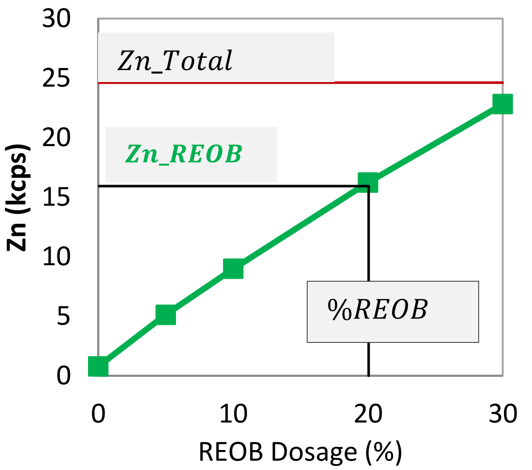


REOB	Benchtop	Handheld
R1	20.6	20.6
R2	30.1	27.6
R3	19.8	20.1
R4	42.4	47.0
R5	28.4	31.5
R6	28.2	27.6
Average	28.3	29.1

Figure 29. Estimation of REOB in an Unknown Seal Coat Binder.

Step 4: Estimate GTR Content Using Zinc Contributed by GTR Alone

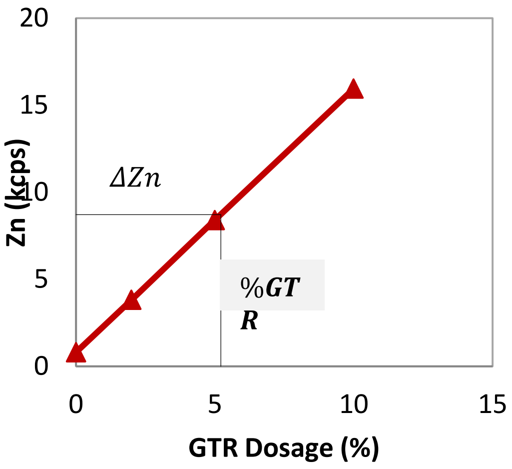
- Estimate Zn contribution from REOB using estimated REOB content and Zn vs. %GTR calibration curve of source binder (see Figure 30).
- Determine: $\Delta Zn = Zn - Zn_{REOB}$.



REOB	Zn_{REOB}	Zn	ΔZn
R1	18.2	24.6	6.5
R2	13.4		11.3
R3	15.9		8.7
R4	13.4		11.3
R5	16.4		8.3
R6	18.4		6.3

Figure 30. Estimation of Zn Contributed by REOB in an Unknown Seal Coat Binder.

- Binder contains REOB only if $\Delta Zn \leq 0$ and contains GTR and REOB both if $\Delta Zn > 0$.
- Calculate GTR content using ΔZn and Zn vs. GTR content calibration curve of GTR-only modified binder (see Figure 31).



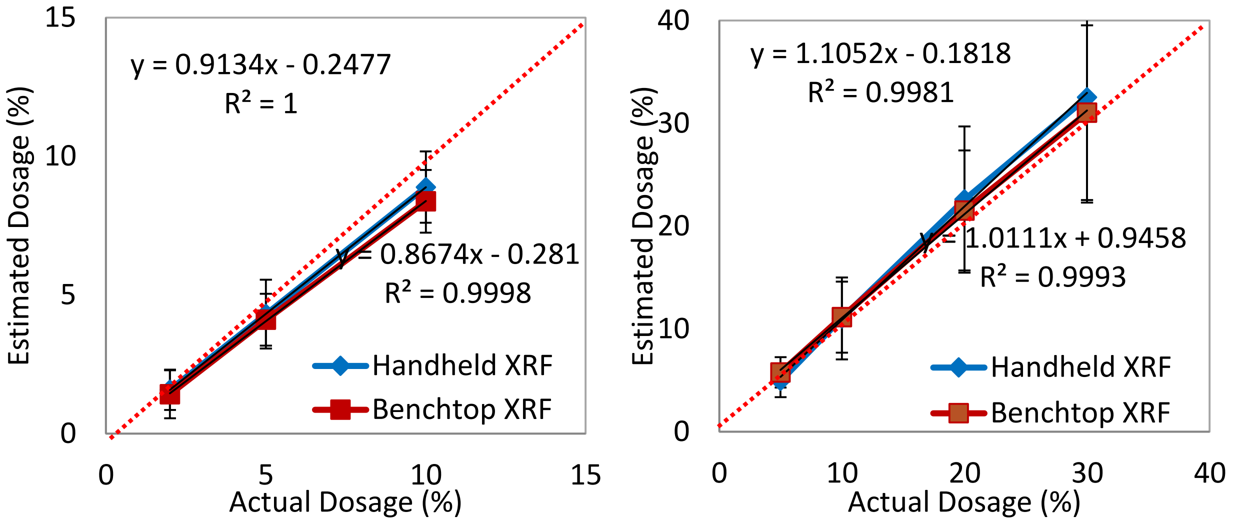
REOB	Zn_{GTR}	%GTR
R1	6.5	3.7
R2	11.3	6.9
R3	8.7	5.2
R4	11.3	6.9
R5	8.3	4.9
R6	6.3	3.6
Average		5.2

Benchtop	Handheld
5.2%	5.4%

Figure 31. Estimation of GTR in an Unknown Seal Coat Binder.

VERIFICATION OF THE DEVELOPED METHOD FOR SEAL COAT BINDERS

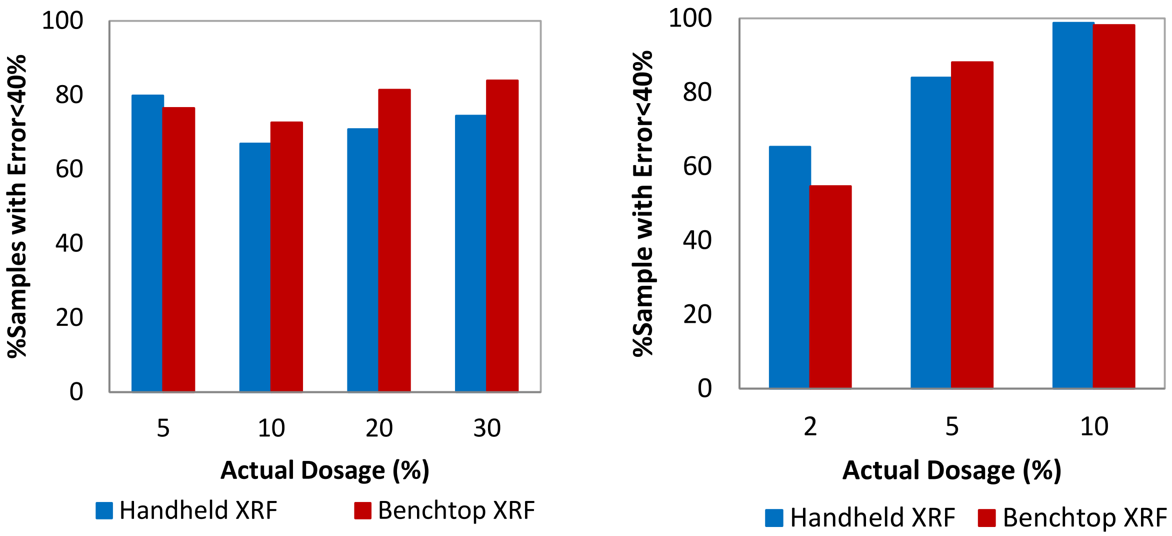
Figure 32 presents average estimated %REOB and %GTR as a function of actual %REOB and %GTR obtained from more than 400 samples used for developing this method. The average %REOB estimated from the handheld and benchtop XRF units are very close to the line of equality and each other. That means, the handheld XRF can be used as a cheaper but equally effective option. The average %REOB estimated from the handheld and benchtop XRFs are slightly below to the line of equality and but very close to each other.



(a) REOB Estimation **(b) GTR Estimation**

Figure 32. REOB and GTR Estimation Method in Seal Coat Binders.

Figure 33 presents the percentages of samples that were estimated with less than 40 percent error. As can be seen, researchers could estimate REOB content with less than 40 percent error in 70–80 percent samples. However, for GTR, the success rate decreases with the benchtop XRF while is acceptable with the handheld XRF. That is, the handheld XRF is better option.



(a) REOB Estimation **(b) GTR Estimation**

Figure 33. Effectiveness of REOB and GTR Estimation Method: Lab Samples.

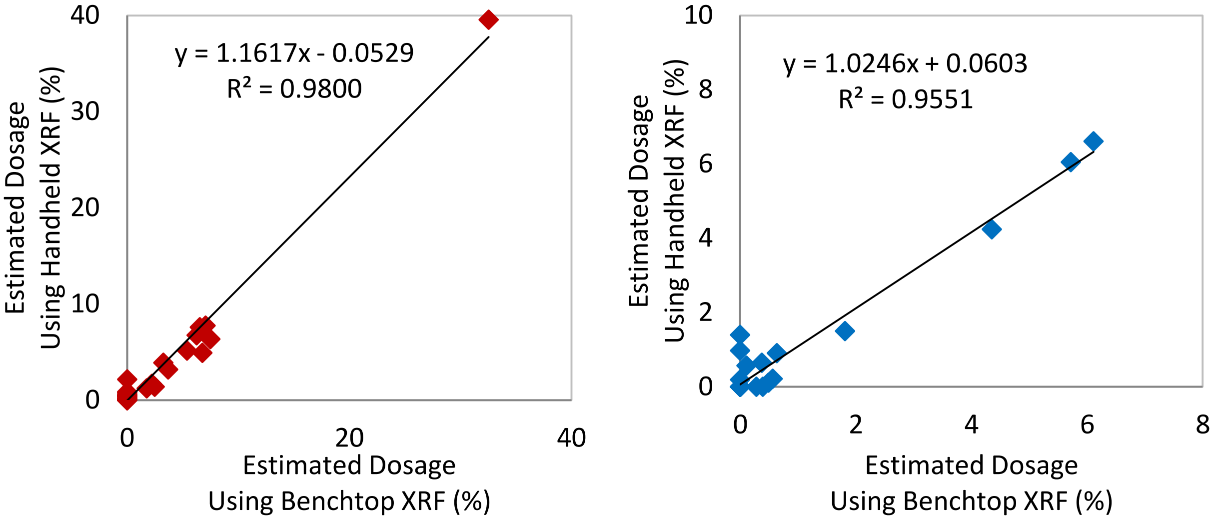
APPLICATION OF THE DEVELOPED METHOD TO SEAL COAT SAMPLES

The methodology was applied to determine %REOB and %GTR in 34 samples provided by TxDOT. Table 17 shows that the estimated REOB and GTR from the handheld XRF were very close to those from the benchtop XRF. Note that one seal coat binder, AC0.6, contains more than 30 percent REOB. Except AC0.6, the maximum %REOB was around 7 percent in the rest of 33 seal coat binders. In terms of GTR, both the handheld and benchtop estimates were very close to each other and close to the actual GTR content.

Table 17. REOB and GTR Estimation in Field Seal Core Binders Samples.

Binder	%GTR		%REOB	
	Benchtop	Handheld	Benchtop	Handheld
AC-5	0.0	0.0	2.5	1.4
AC-5	0.0	0.0	0.0	0.0
AC-0.6	0.0	0.0	0.0	0.1
AC-1.5	0.0	0.0	0.0	0.2
AC-3	0.0	0.0	0.0	0.5
AC-15P	0.6	0.9	3.3	3.9
AC-20-5TR	4.4	4.2	0.0	0.0
AC-0.6	0.0	0.0	7.5	6.4
AC-10-2TR	1.8	1.5	0.0	0.0
AC-20-XP	0.0	0.0	2.2	1.7
AC-15P	0.0	0.0	0.0	0.6
AC-20-5TR	5.7	6.1	0.0	0.3
AC-5	0.4	0.0	0.0	0.4
AC-15P	0.6	0.2	0.0	0.1
AC-10	0.0	0.0	0.0	0.8
AC-15P	0.0	0.0	0.0	0.0
AC-20-XP	0.0	0.0	1.8	1.2
AC-0.6	0.5	0.1	5.4	5.2
AC-1.5	0.0	1.0	6.3	6.7
AC-3	0.3	0.0	0.0	2.1
AC-5	0.0	0.0	0.0	0.5
AC-10	0.0	0.0	0.0	0.8
AC-15P	0.0	0.0	0.0	0.2
AC-20-5TR	6.1	6.6	0.0	0.0
AC-10	0.0	0.0	0.0	0.2
AC-10	0.0	0.0	0.0	0.0
AC-0.6	0.4	0.6	32.5	39.6
AC-5	0.1	0.6	7.1	7.7
AC-10	0.0	0.2	3.7	3.2
AC-15P	0.0	0.0	6.5	7.6
AC-20-XP	0.0	1.4	6.8	4.9
AC-3	0.0	0.0	0.0	0.5
AC-5	0.0	0.0	0.0	0.4
AC-10-2TR	0.0	0.0	0.0	0.4

Figure 34 shows cross plots of the estimated REOB and GTR contents from the benchtop XRF and the handheld XRF measurements. Overall, the handheld XRF based method can estimate REOB content with almost similar effectiveness and accuracy as the benchtop XRF based method.



(a) REOB Estimation **(b) GTR Estimation**

Figure 34. REOB and GTR Estimation in Field Seal Core Binders Samples.

SUMMARY

This chapter focused on detecting REOB in seal coat binders. Two methods were developed and verified: one using a three-step benchtop WDXRF spectroscopy technique and the other with a two-step handheld EDXRF spectroscopy technique. From this study, the following conclusions could be drawn:

1. S and V are always present in seal coat binders, implying the normalized S and V plot can be used to identify source of binder as before.
2. Si is present more significantly in GTR than in seal coat binders, polymer, and REOB. However, their intensities and corresponding concentrations in REOB-modified blends are quite small. Therefore, it is not used to estimate GTR in this study even though a previous study suggested otherwise.
3. Zn was present in minimal amount in seal coat binders, moderate amount in REOB, but significant amount in GTR, implying the contribution of each of these materials to Zn concentration/intensity needs to be separated to determine their individual percentage.
4. Zn/Ca ratio has opposite relationships with the increase in the percentage of REOB and GTR. The ratio increases with an increase in GTR content but decreases with an increase in REOB content. As such, Zn/Ca ratio can be used to identify whether seal coat binders have been modified with GTR alone or not.
5. The normalized S vs. V plot of seal coat binders and the analysis of closeness parameter can be used to select possible sources of binder.
6. Binders blended with GTR only do not contain any Mo. As such, the measured value of Mo intensity or concentration and the calibration curve of Mo belonging to the standards

can be used to estimate the REOB content in a given binder that was modified with REOB alone or together with GTR.

7. The REOB content estimated using Mo can be further used to determine intensity or concentration of Zn contributed by REOB. If this estimated value is smaller than the measured intensity or concentration of Zn, it can be hypothesized that binder must have been modified with REOB and GTR together. In such cases, the difference in measured and estimated intensities or concentrations of Zn can be used to determine the percentage of GTR in the binder using the Zn-calibration curve of the source binder.
8. REOB/GTR contents estimated from both the handheld and the benchtop XRF-methods are close to the actual REOB/GTR contents and to each other.

CHAPTER 5: IMPACT OF REOB ON ASPHALT BINDER PROPERTIES

REOB is the re-refined engine oil bottom rather than asphalt binder. Pavement engineers have expressed serious concerns on the performance of the binder/REOB blends in terms of PG grade, rheological and chemical properties, aging resistance, and microstructure. This chapter details the work performed to study how REOB affect binder properties and how significant these effects, if any, are.

OVERVIEW OF MATERIAL SELECTION AND LABORATORY TESTS

Six PG64-22 binders from different binder suppliers, one PG58-28 binder, and one recycled binder were blended with six REOB and one PPA at different proportions. Table 18 presents the list of these materials. Also an aromatic extract (AE) and a bio-rejuvenator (BR) are included in the list as modifiers.

Table 18. List of Materials Used to Study the Impact of REOB on Binder Properties.

Material	Source	PG	Notation
Asphalt Binder	#1	64-22	A6422
	#2	64-22	B6422
	#3	64-22	C6422
	#4	64-22	D6422
	#5	64-22	E6422
	#6	64-22	G6422
		58-28	G5828
Extracted Binder	#1	94-xx	RAP
REOB	#1	n/a	R1
	#2		R2
	#3		R3
	#4		R4
	#5		R5
	#6		R6
PPA	#1	n/a	P1
AE	#1	n/a	AE
BR	#1	n/a	BR

The blends were prepared by first heating the binders at their specific mixing temperature and then doping them with selected modifier(s) (up to 20 percent REOB/BR/AE, up to 2 percent PPA, and up to 15 percent RAP-extracted binder by total weight of blend). The blends were thoroughly stirred and reheated for three times in total for homogeneity.

The blend was then subjected to short-term aging in a rolling thin film oven (RTFO) at 325°F (163°C) for 85 minutes. RTFO-aged blends were finally subjected to long-term aging in a pressure aging vessel (PAV) at 100°C and 2.2kPa for 20, 40, or 80 hours.

Various binder tests, as shown in Table 19, were conducted on these blends to investigate the effects of REOB, PPAs, AE, and BR on their properties.

Table 19. List of Selected Binder Tests.

Binder Tests	References	Parameters
Mechanical Property Tests		
PG Tests		
Dynamic Shear Rheometer	AASHTO T315-12	High Temperature PG
	AASHTO M320-10	
	AASHTO T313-12	Low Temperature PG
BBR	AASHTO M320-10	$\Delta T_c = T_{cs} - T_{cm}$
Frequency Sweep Tests **Dynamic Shear Rheometer**	Anderson et al. (2011)	Crossover Frequency: ω_c Rheological index: R
Chemical Property tests		
Fourier Transform Infrared Spectroscopy Tests	Jemison et al. (1992) Glover et al. (2005)	Carbonyl Area: CA
Saturate-Asphaltene-Resin-Aromatic Fraction Tests	IP469: 2001 (2006)	SARA Concentrations
Microstructural Tests		
Atomic Force Microscopy Tests	Planche et al. (2015)	Microstructure

IMPACT OF REOB ON BINDER HIGH TEMPERATURE PG GRADE

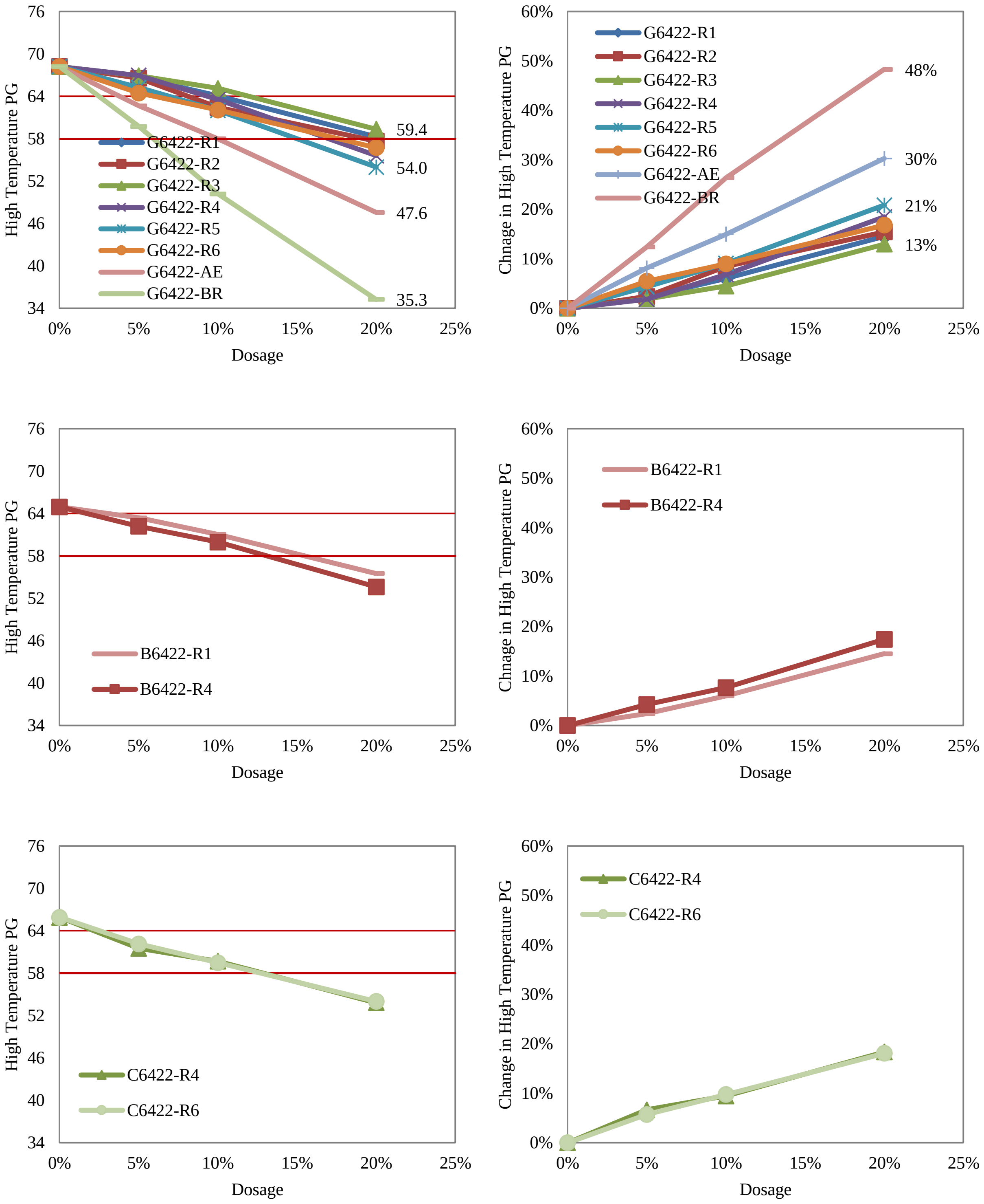
Dynamic shear rheometer tests of binders were conducted to determine the potential impact of REOB (R1–R6), PPA (P1), AE, and BR on base binder PGs following AASHTO T 315-12. The tests were conducted on unaged (i.e., OB) and RTFO-aged samples for each blend using the Malvern Kinexus Pro+ instrument.

Figure 35(a) presents the high temperature PG of samples prepared by blending PG64-22 binder with different dosages of modifiers (i.e., REOB, AE, and BR). The figure clearly shows that each of these modifiers can reduce the high temperature PG of base binder, confirming any of these modifiers can be used as softening agents. However, the figure also shows that the degree of this effect totally depends on modifier type and source, meaning modifier obtained from one source may be more effective than the one obtained from another source. Figure 35(a) also shows that the selected AE is more effective than all the six REOB, but less effective than the selected BR in changing high temperature PG of the base binders.

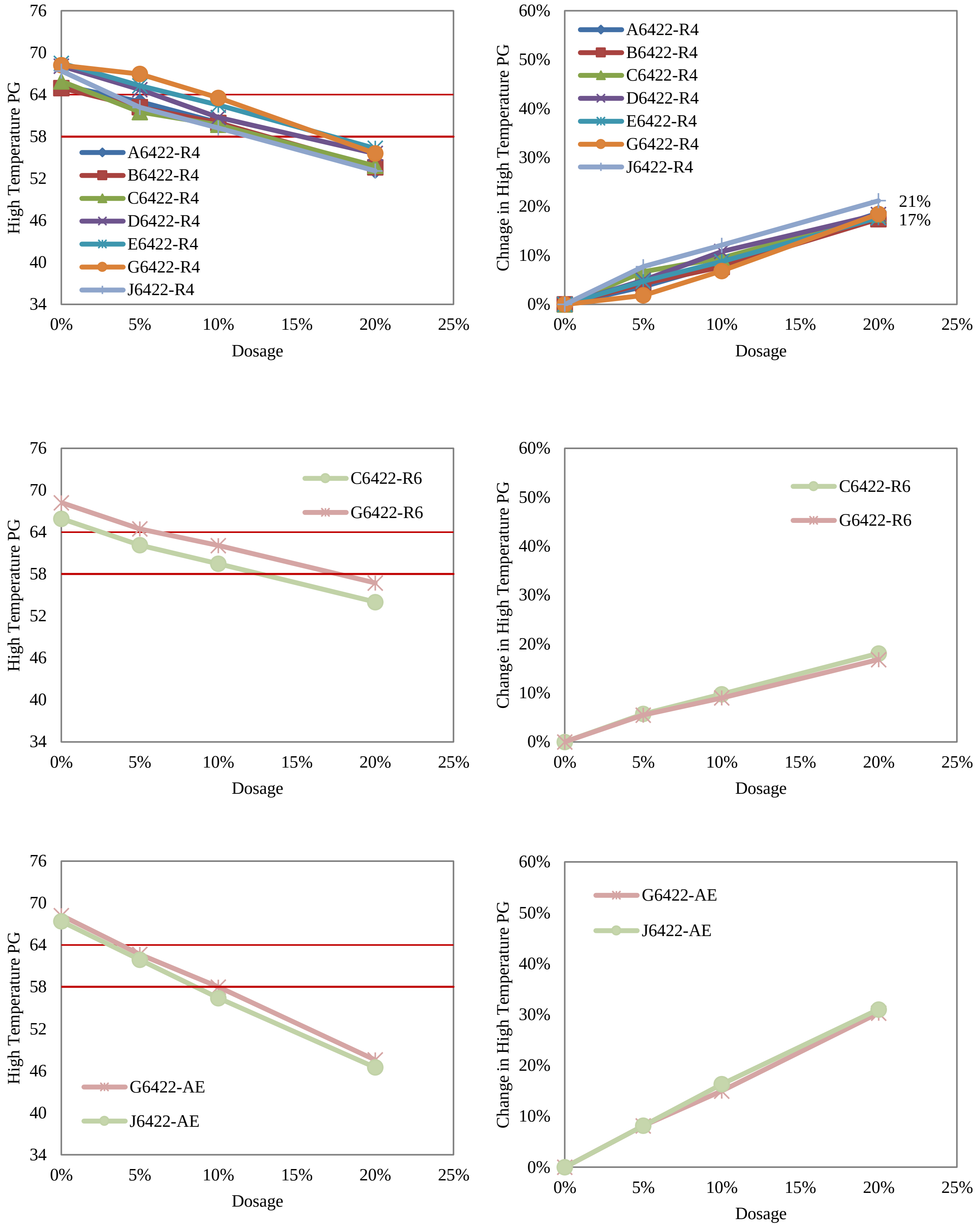
Figure 35(b) presents the high temperature PG of samples prepared by blending different PG64-22 binders with different dosages but the same source of modifier. The figure once again demonstrates that high temperature PG decreases with the increase in REOB dosage, reconfirming the softening effect of REOB on asphalt binders. Additionally, the figure also shows that the percentage reduction differs with the source of binder for any given dosage rate, which suggests that not all binders are influenced equally by the same source of REOB. This observation explains why different binder sources use different REOB to modify base binders.

Comparing Figure 35(a) with Figure 35(b), it can be seen that the source of REOB has more pronounced effect on high temperature PG of base binder than the source of binder itself.

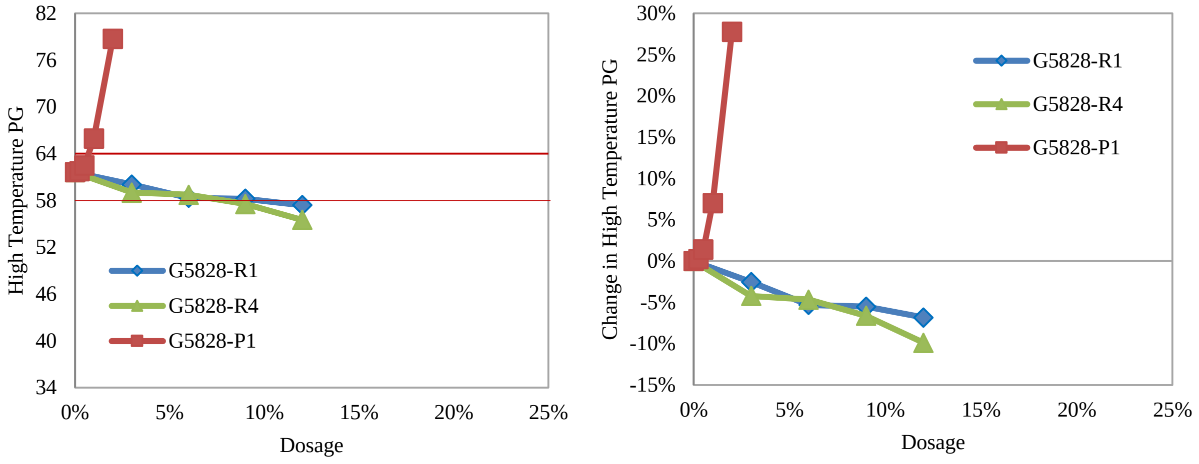
Furthermore, researchers evaluated the combined effect of REOB and PPA. Figure 35(c) presents the high temperature PG of binder samples prepared by blending a PG58-28 binder with different dosages and sources of REOB and different PPA dosages. The figure illustrates that REOB and PPA have quite opposite effect on high temperature PG of binders. REOB reduces the high temperature PG while PPA increases its value. This signifies the fact that PPA acts as a stiffening agent while REOB acts as a softening agent. The figure also demonstrates that same amount of PPA is considerably more effective in changing high temperature PG than the same amount of REOB. In other words, a much smaller amount of PPA, when compared to REOB, is required for changing the high temperature PG of base binder. These facts suggest that target high temperature PG specification can be met by treating base binders either with a higher dosage of REOB together or a much smaller dosage of PPA.



(a) Same PG64-22 binder + different REOB



(b) Different PG64-22 binders + same REOB



(c) Same PG58-28 binder + different REOB/PPA

Figure 35. High Temperature PGs of Unmodified and REOB/PPA-Modified Binders.

IMPACT OF REOB ON BINDER LOW TEMPERATURE PG GRADE

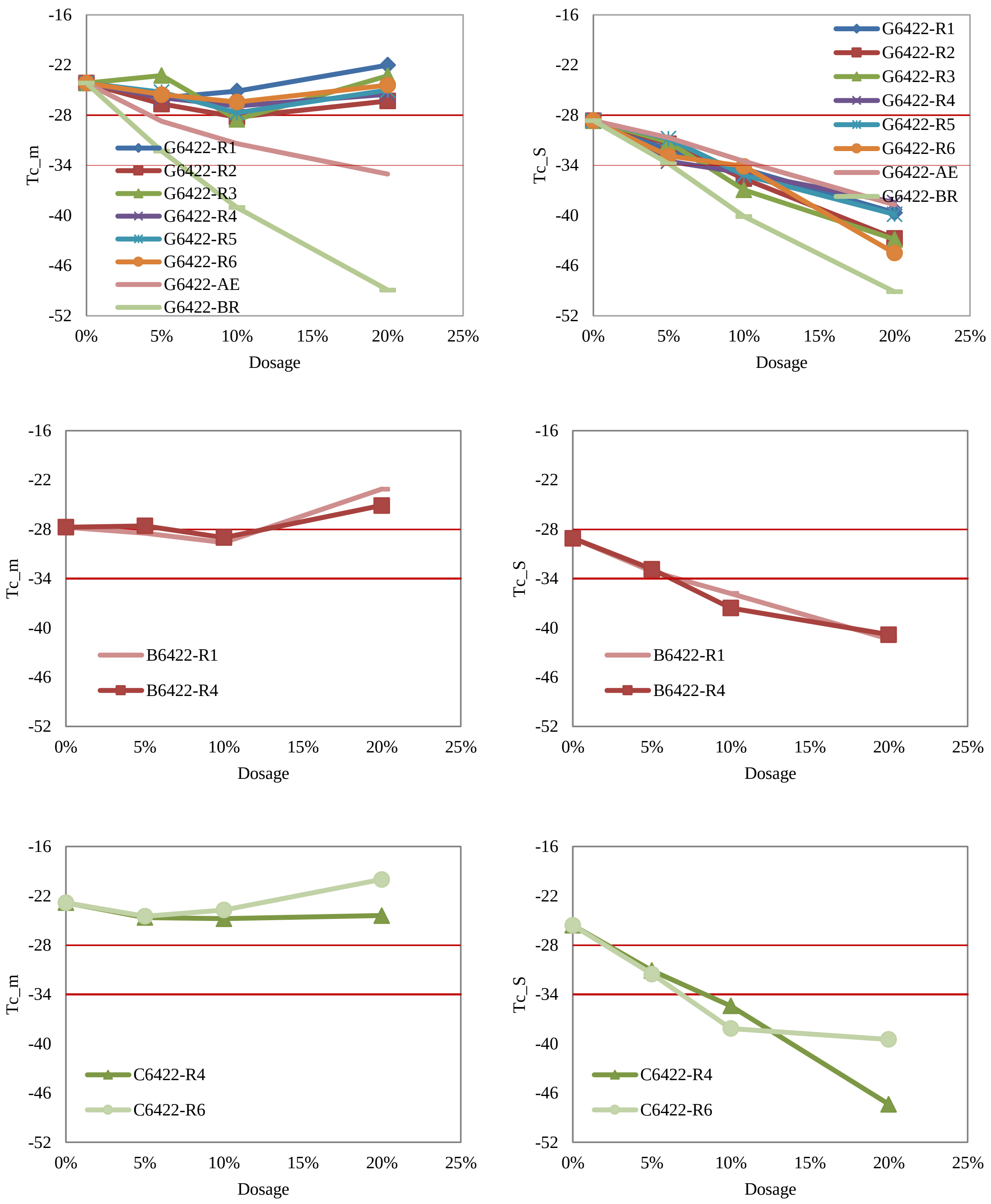
BBR tests of binders were conducted to determine the potential impact of REOB and other modifiers on low temperature PG of base binders (AASHTO T 313-12). The tests were conducted on PAV-aged samples of each blend using the Cannon Instruments TE-BBR instrument. Samples were conditioned at desired test temperatures for an hour before the tests.

Figure 36(a) presents measured values of creep slope- and creep stiffness-based critical low temperature PGs of samples prepared by blending the same PG64-22 binder with different dosages and sources of REOB, one AE, and one BR. Figure 36(b) presents $T_{c-m}$and T_{c-S} of samples prepared by blending various PG64-22 binders but same source of modifier.

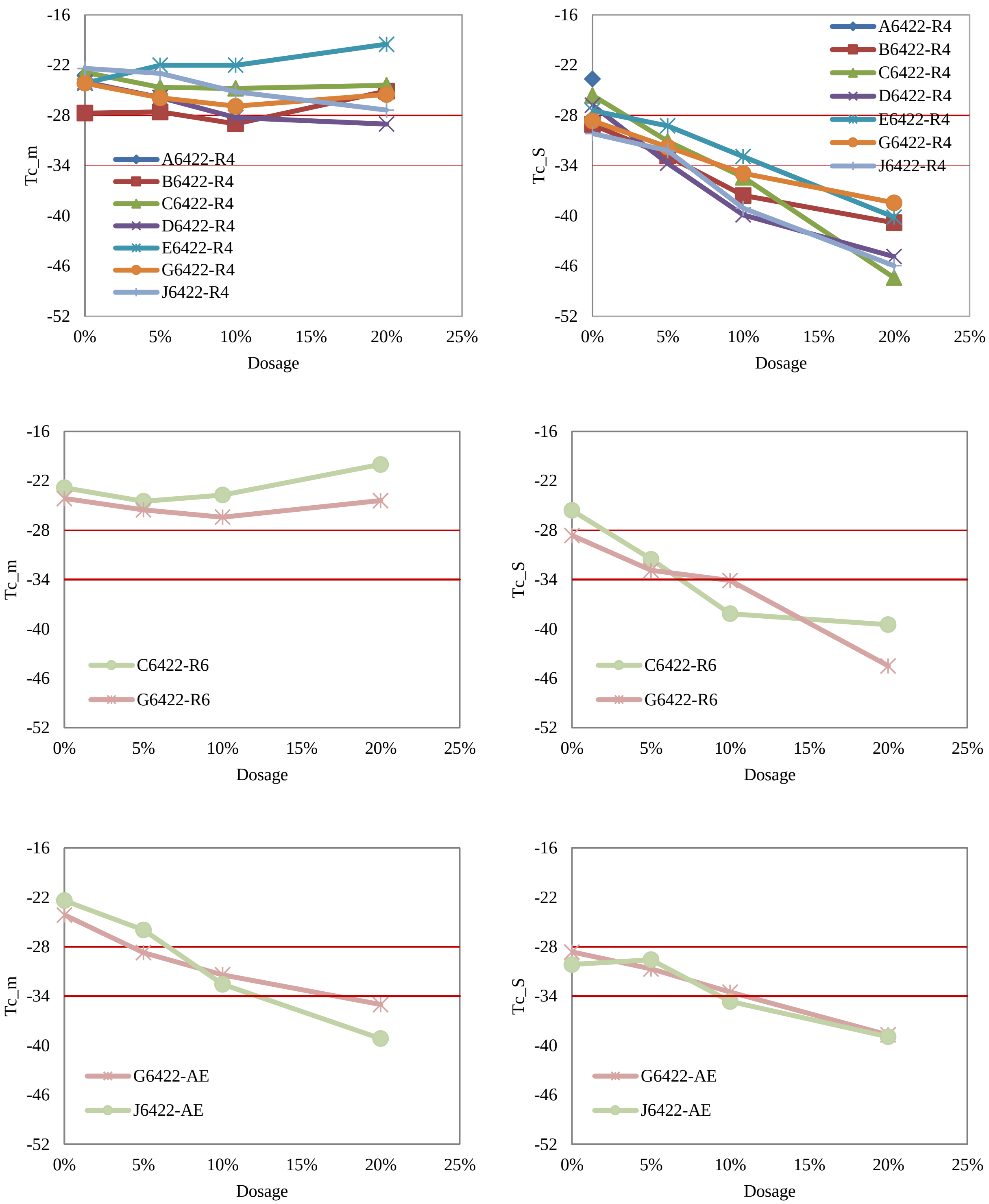
Figure 36(a) and Figure 36(b) show that the REOB reduces the value of T_{c-S} more significantly than T_{c-m}. The figures also indicate that T_{c-m} is always greater than T_{c-S}, and therefore controls the low temperature PG of the binders modified with REOB. This observation suggests that even though REOB can reduce the stiffness of base binders, they may not necessarily improve relaxation properties of binders. In other words, REOB are more effective in lowering the overall stiffness of binders than making them capable of relaxing stresses faster. Ideally, a binder with good relaxation property is more preferred.

Figure 36(a) and Figure 36(b) also show that selected AE and BR were more effective than any REOB in changing low temperature PG. Even a small percentage of these materials could lower the PG by one grade whereas even a high percentage of REOB could not do in many cases. Since T_{c-m} of REOB-modified binder controls the low temperature PG while not changing its absolute value drastically even at higher dosage rates, binder suppliers can use as much REOB as possible to meet the binder purchase specifications as long as they can control high temperature PG, which may potentially explain the reason for high intensity of low temperature (non-load induced) cracking observed in pavements constructed with REOB-modified binders.

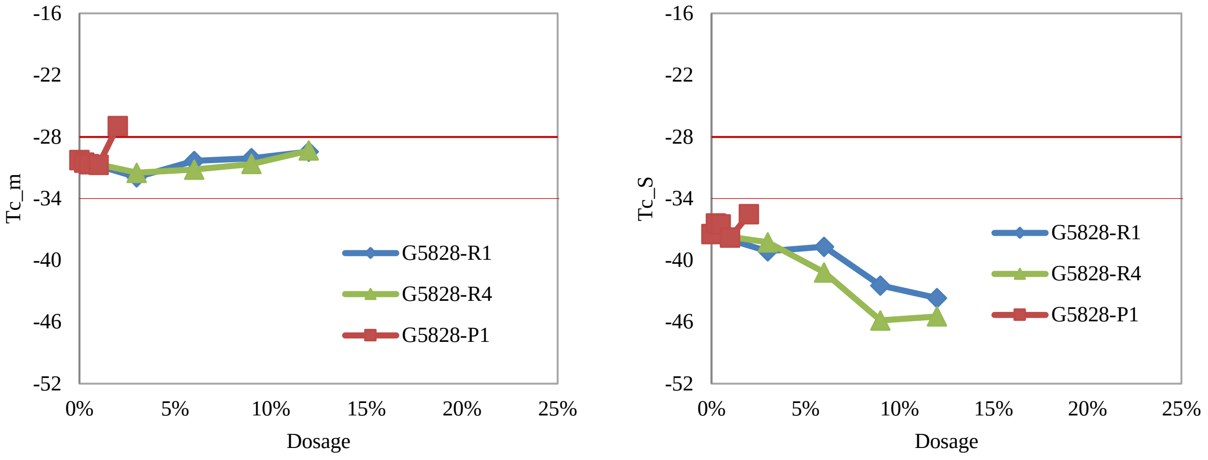
Figure 36(c) presents $\mathrm{T_{c-m}}$ and $\mathrm{T_{c-S}}$ values of samples prepared by blending a PG58-28 binder and a PPA with different dosages and sources of REOB. The figure clearly illustrates that REOB and PPA have quite opposite effect on $\mathrm{T_{c-m}}$ and $\mathrm{T_{c-S}}$ as they did on high temperature PG. The figure also shows that $\mathrm{T_{c-m}}$ controls the low temperature PG of these blends. Like before, the figure also reconfirms that same amount of PPA is more effective in changing low temperature PG than the same amount of REOB.



(a) Same PG64-22 binder + different REOB



(b) Different PG64-22 binders + same REOB



(c) Same PG58-28 binder + different REOB/PPA

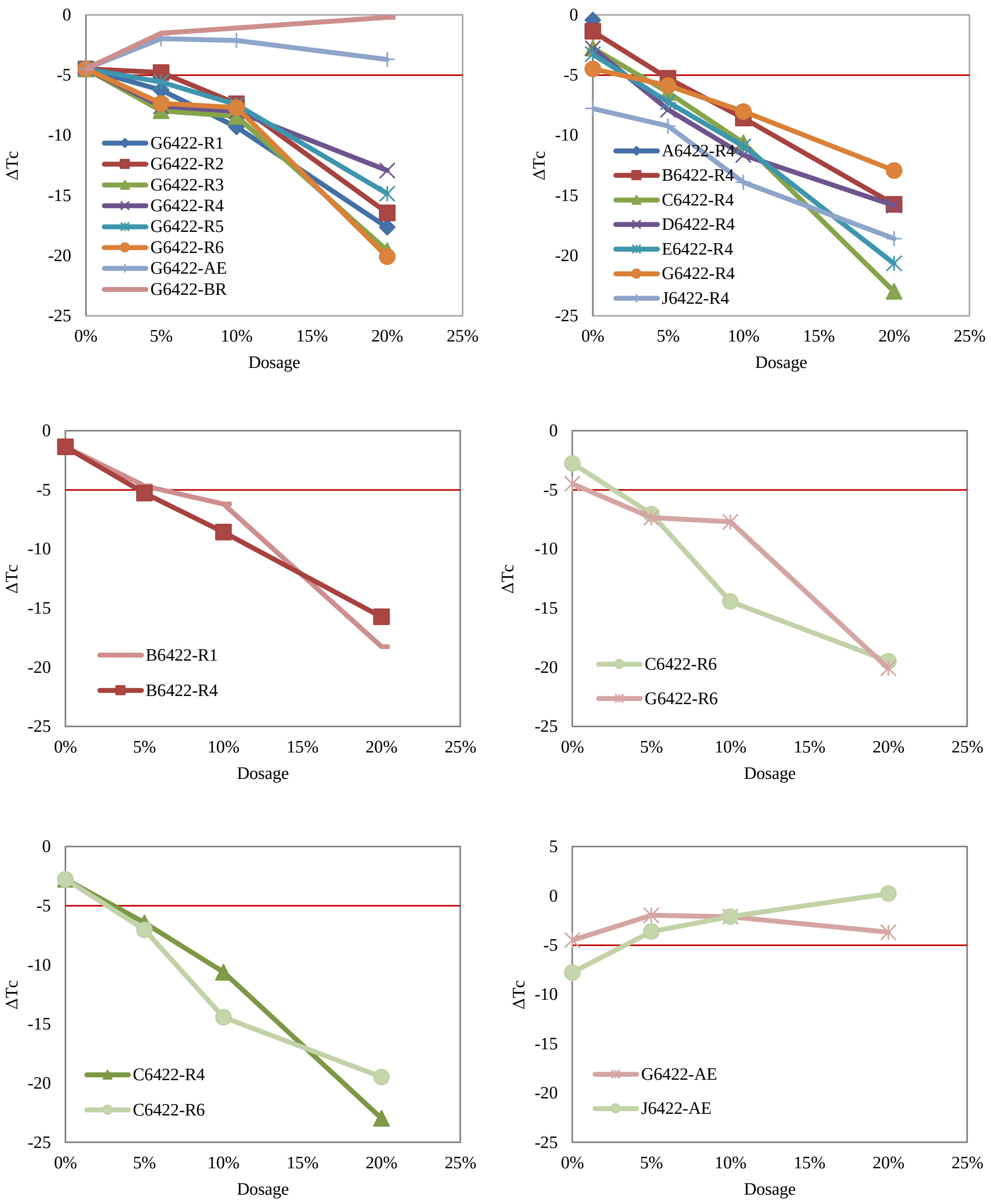
Figure 36. Low Temperature PGs of Unmodified and REOB/PPA-Modified Binders.

IMPACT OF REOB ON ΔT_c

In last several years, the difference in critical low temperature obtained from creep stiffness and creep slope (i.e., $\Delta T_c = T_{c-S} - T_{c-m}$) measured from BBR tests has been discovered to be an indicator for asphalt binder quality. Recent studies suggested of limiting ΔT_c at −2.5°C or −5.0°C to avoid severe cracking (Bennert et al. 2016; Li et al. 2016). This study employs ΔT_c to evaluate potential impact of REOB, PPA, AE, and BR on binder quality.

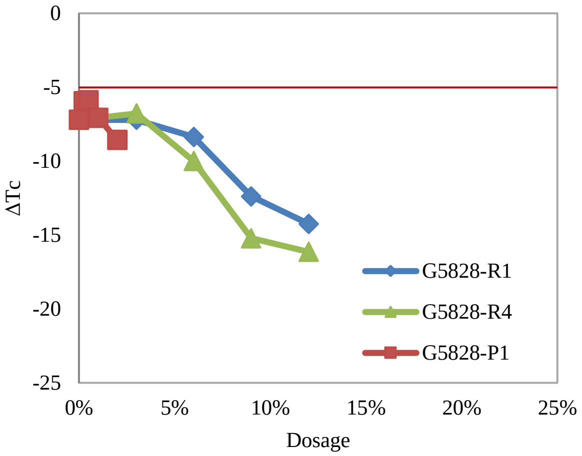
Figure 37(a) and Figure 37(b) present the ΔT_c values of samples prepared by blending PG64-22 binders with REOB, AE, and BR at different percentages. Similarly, Figure 37(c) presents the ΔT_c values of samples prepared by blending PG58-28 binder with REOB and PPA at different proportions. Figure 37 clearly shows that ΔT_c becomes more negative with an increase in REOB or PPA dosage. This trend was observed irrespective of the source of binder and type of modifier (i.e., REOB or PPAs). However, the trend reversed when AE or BR was used to modify binders instead.

The fact that both PPA and REOB made ΔT_c more negative (i.e., ΔT_c of PPA- and REOB-modified binders < ΔT_c of unmodified binders) with an increase in their dosages suggests that the use of significantly high percentage of REOB or PPA can make binders less capable of relaxing stress at low temperature, and thereby more prone to cracking. Inversely, the fact that AE and BR made ΔT_c less negative (i.e., ΔT_c of AE or BR modified binders > ΔT_c of unmodified binders) with an increase in their dosages implies that binders modified with AE or BRs make binders more capable of relaxing stress at low temperature, and thereby less prone to cracking.



(a) Same PG64-22 binder source + different REOB sources

(b) Different PG64-22 binder sources + same REOB/AE sources



(c) Same PG58-28 binder source + different REOB/PPA sources

Figure 37. ΔTc Values of Unmodified and REOB/PPA-Modified Binders.

IMPACT ON RHEOLOGICAL PROPERTIES

Frequency sweep tests were conducted to determine the potential impact of REOB, AE, and BR on the rheological properties of base binders. The tests were conducted on unaged, RTFO-aged, and one, two, or four times PAV-aged samples using the dynamic shear rheometer mentioned above. The tests were carried out by subjecting 25 mm diameter × 1.0 mm thin binder samples to 1.0 percent shear strain from 0.1 rad/sec to 100 rad/sec at 80°C, 40°C, and 20°C using 25-mm parallel plate geometry, and 8-mm diameter × 2.0 mm thin binder samples to 0.1 percent shear strain from 0.1 rad/sec to 100 rad/sec at 20°C, 0°C, and −10°C. From these tests, complex shear modulus (G^*) and angular frequency(ω) data were obtained as illustrated in Figure 38(a). These parameters were used to construct master curves at a reference temperature, T_r of 45°C using the Christensen-Anderson (Christensen and Anderson 1992) and the Willaims-Landel-Ferry models (Ferry 1980; Williams et al. 1955):

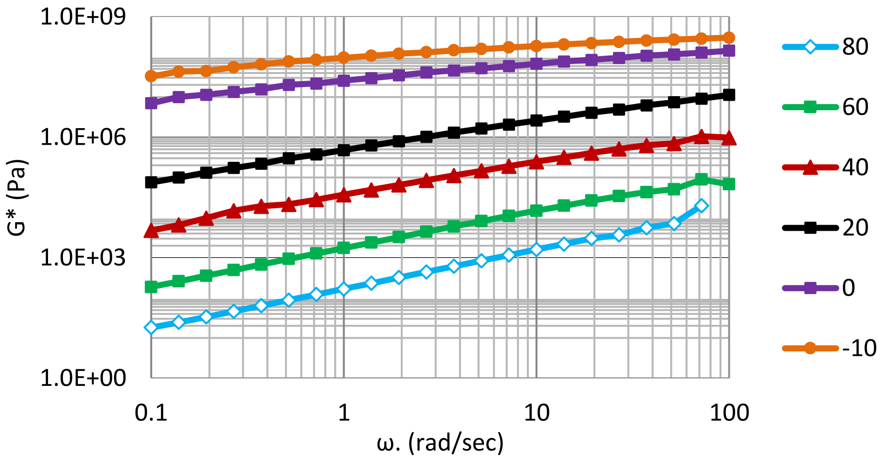
$$G^*(\omega_r) = G_g\left[1+\left(\frac{\omega_c}{\omega_r}\right)^{\frac{\log 2}{R}}\right]^{-\frac{R}{\log 2}} \tag{3}$$

$$\delta(\omega_r) = 90\left[1+\left(\frac{\omega_c}{\omega_r}\right)^{\frac{\log 2}{R}}\right] \tag{4}$$

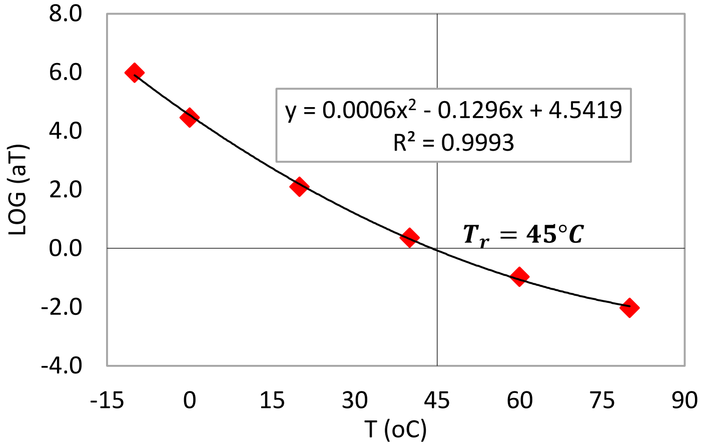
$$\log[a_T] = -C_1\left[\frac{T-T_r}{C_2+T-T_r}\right] \tag{5}$$

Herein, $\omega_r, \omega_c, R,$ and G_g refer to reduced frequency, crossover frequency, rheological index, and glassy modulus (typically 1.0 GPa in shear), respectively. The parameter, a_T , refers to the shift factor at temperature, T , and the parameters C_1 and C_2 refer to fitting constants related to temperature susceptibility. Figure 38(b) illustrates the relationship of shift factors with temperature; Figure 38(c) presents the master curve constructed by shifting the curves in Figure 38(a) using the relationship from Figure 38(b) for binder B6422.

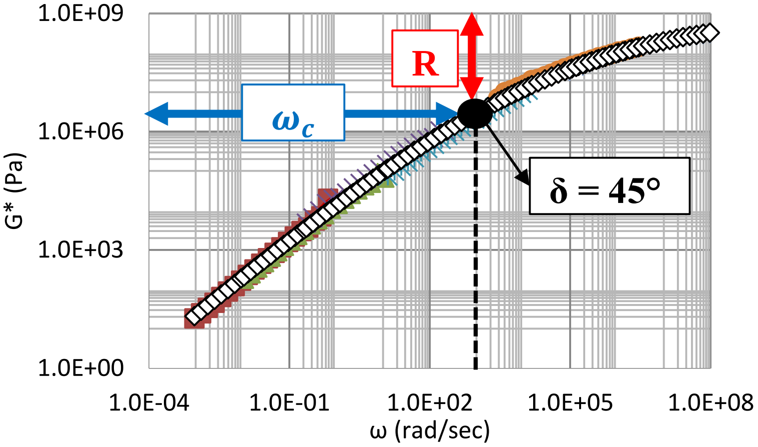
From these tests, crossover frequency, ω_c, and rheological index, R, were extracted to evaluate rheological properties of modified and unmodified binders. Crossover frequency, ω_c, is an indicator of general consistency or hardness at selected temperature, and is defined as the frequency at a given temperature where storage and loss moduli are equal (i.e., where phase angle is 45° [see Figure 38(c)]) (Anderson et al. 2011). R is a shape factor of master curve and is defined as the difference between the logarithmic values of the glassy modulus and the dynamic complex modulus at the crossover frequency [see Figure 38(c)]. It primarily describes how efficiently binders transfer from elastic state to viscous (steady) state (Anderson et al. 2011). Higher R value refers to a flatter master curve and a slower elastic-to-steady state transition and vice versa. Therefore, a binder with lower R (i.e., faster transition) and higher ω_c (i.e., softer) is more resistant to cracking. With aging or with the use of RAP, ω_c-value increases while R-value decreases. This trend is reverses itself when BRs are used (Karki and Zhou 2016). The black-space diagram of ω_c and R can be used to study the effect of modifiers such as REOB, rejuvenators, and aging on overall hardness and elastic-to-steady-state transition properties of base binders (Karki and Zhou 2016; Mogawer et al. 2017).



(a) Frequency Sweep Test Results



(b) Shift Factor Used to Construct the Master Curve



(c) Illustration of Rheological Parameters on a Master Curve

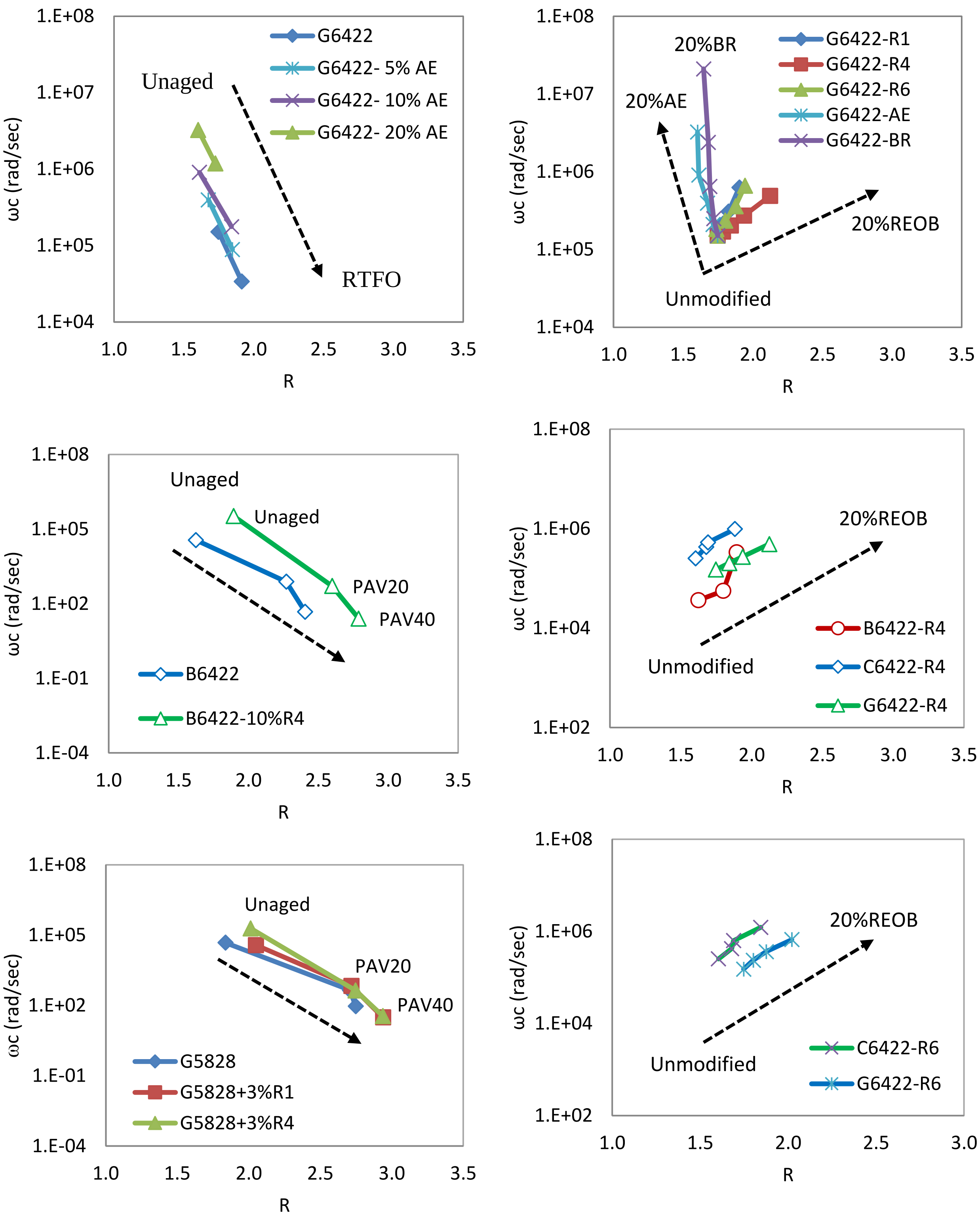
Figure 38. Illustration of Master Cure Construction and Rheological Properties.

Figure 39(a) and Figure 39(b) present the black space diagrams of crossover frequency and rheological index of binders at different aging and modification levels. Figure 39(a) shows that an increase in oxidation (or aging) reduces the value of crossover frequency but increases the value of rheological index, consequently elevating their overall stiffness while making their elastic-to-steady-state transition slower (i.e., making them less sensitive to loading rate and temperature). These correlations with aging were observed irrespective of the change in binder source and grade (G5828, G6422, and B6422), REOB source (R1, R4), REOB dosage (0 percent, 3 percent, and 10 percent), and AE dosage (0 percent, 5 percent, 10 percent, and 20 percent)

Figure 39(b) shows that an increase in REOB content increases the values of both the crossover frequency and the rheological index consequently lowering their overall stiffness and making their elastic-to-steady state transition slower. These impacts were observed irrespective of the change in the source of binder (G6422, B642, and C6422) and REOB (R1, R4, and R6). These results strongly suggest that the REOB and aging have completely opposite effect on binder stiffness but quite similar effect on elastic-to-steady state transition—a potentially important factor that can be linked to reported higher degree of crack severity reported in pavements constructed with REOB-modified binders despite binders meeting the purchase specifications.

Figure 39(b) also shows that AE and BR both increased the value of crossover frequency but decreased the value of rheological index, thereby lowering their overall stiffness while also making elastic-to-steady-state transition faster (i.e., making them more sensitive to loading rate and temperature). These results strongly suggest that REOB, AE, and BR have similar effect on binder stiffness (i.e., softening effect) but have opposite effect on elastic-to-steady state transition.

Table 20 presents the summary of these test results. The table clearly shows REOB, AE, and BR all soften but aging hardens the binders. In terms of letting binders reach steady (viscous) state from elastic state, aging and REOB are more effective than AE and BR. The other very important thing is REOB cannot be used as a rejuvenating agent.



(a) Effect of Aging **(b) Effect of Modifier**

Figure 39. Black Space Diagram of Unmodified and REOB/PPA-Modified Binders.

Table 20. Summary of Effect of Modifiers on Rheological Properties of Binders.

Factor	ω_c	Stiffness	R	Master Curve Shape	Change from Elastic State to Viscous (Steady) State
Aging	-	Hardens	+	Flatter	Ineffective
REOB	+	Softens	+	Flatter	Ineffective
AE	+	Softens	-	Sharper	Effective
BR	+	Softens	-	Sharper	Effective

IMPACT ON CHEMICAL AGING PROPERTIES

Fourier-transform infrared-attenuated total reflectance spectroscopy tests were conducted to determine the potential impact of REOB on chemical aging potential properties of base binders. The impact was evaluated by calculating the area between wave numbers 1820/cm and 1650/cm in an infrared absorption spectrum. This particular area refers to the amount of infrared light absorbed by compounds belonging to carbonyl group. Carbonyl group is a functional group composed of a carbon atom double bonded with an oxygen atom, denoted as C=O. An increase in carbonyl area refers to increased level of aging (Glover et al. 2005; Jemison et al. 1992). As such, the absolute value of carbonyl area and the change in its value were used to evaluate the effect of REOB and PPA sources and concentrations on chemical aging properties of binders.

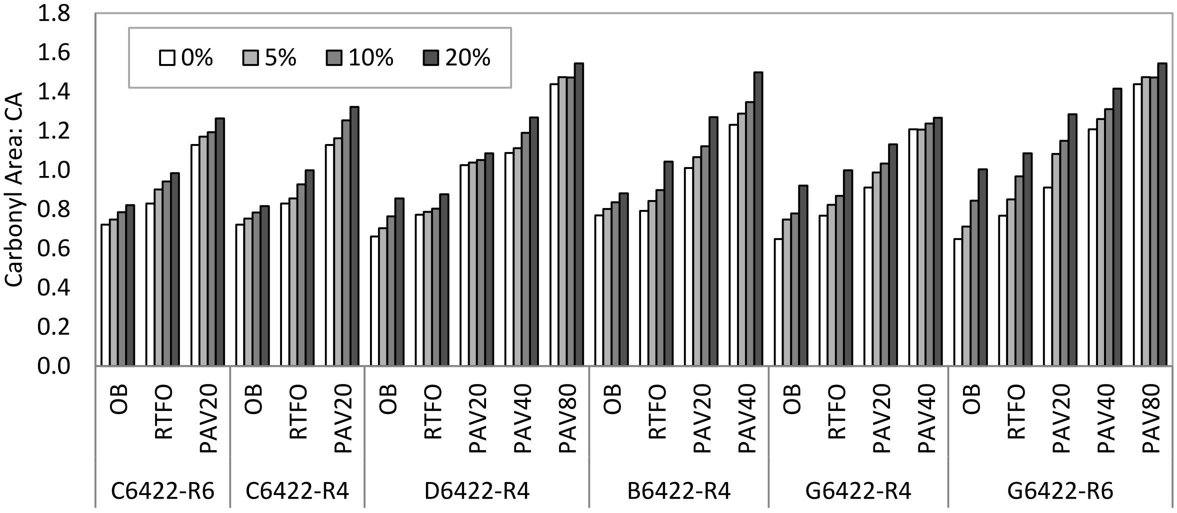
Figure 40(a) presents the FTIR test results of blends prepared with different combinations of binder and REOB obtained from different sources at five different levels of aging (Unaged, RTFO-aged, RTFO+PAV20, RTFO+PAV40, RTFO+PAV80). The figure clearly shows that carbonyl area increases with aging for any given binder source, REOB source, and REOB dosage. Since REOB and binders themselves contain C=O groups, absolute values of carbonyl area in each blend were normalized for carbonyl area of unmodified and unaged binders to better understand actual influence of REOB on aging potential of binders.

Figure 40(a) also shows that carbonyl area in unmodified binder after a certain duration of aging became equivalent to the carbonyl area in binder unaged binder modifier with a certain amount of REOB. For example, unmodified, RTFO-aged C6422 and 20 percent REOB-modified, unaged C6422 binder registered carbonyl area values of 0.83 and 0.82, respectively. This suggests that aging and addition of REOB might have negative effects on ability of binders to further age.

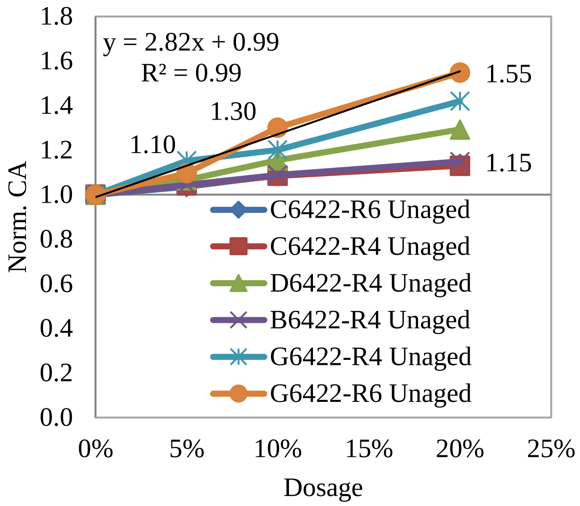
Figure 40(b) presents the normalized values of carbonyl area in unaged and aged blends for normalized carbonyl area in unmodified binders (i.e., carbonyl area of x% REOB / carbonyl area of base binder). This figure clearly demonstrates that normalized carbonyl area increased with an increase in REOB dosage irrespective of aging levels. For example, normalized carbonyl area in G6422-R6 blends increased at a rate of 0.35 per REOB% after 80 hours of PAV aging, which originally increased at a rate of 2.82 per REOB% before any aging. The figure also suggests that after certain level of aging, there is minimal difference in normalized carbonyl areas of binders blended with higher and lower dosages of REOB. This suggests the binders modified with higher dosages of REOB could no longer age due to high concentration of carbonyl area already in them. For example, normalized carbonyl area in blends prepared with the G6422 binder and the R6-REOB measures 1.10 at 5 percent, 1.30 at 10 percent, and 1.55 at 20 percent when there was no aging involved. It reduced to a value close to 1.07 when it was PAV aged for 80 hours. An ideal binder would age perpetually but at a very slow rate, which is not the case with REOB-modified binders.

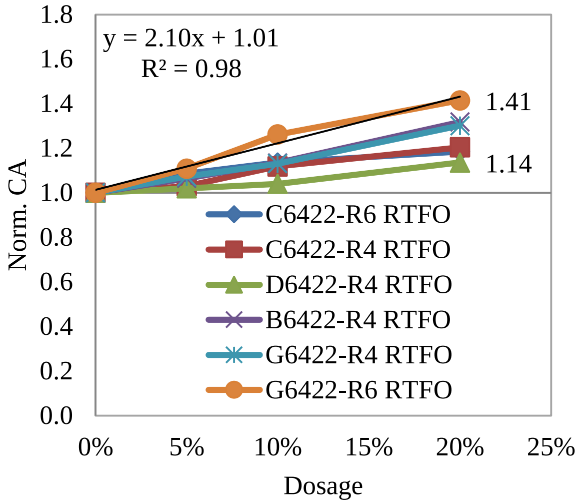
Figure 40(c) presents the normalized values of carbonyl area in blends aged for four different durations (i.e., RTFO+PAV0, RTFO+PAV20, RTFO+PAV40, and RTFO + PAV80) for the carbonyl area in unaged binder. The figure clearly demonstrates that carbonyl area increased with elevated level of aging. However, the figure also shows that the rate of increase reduced with higher dosage of REOB. For example, unmodified, 5 percent, 10 percent, and 20 percent R6-modified G6422 binder registered decrease in carbonyl area at 0.0164, 0.0136, 0.0111, and 0.0098 per PAV hour. Additionally, the figure also shows sources of binders and REOB both affect this increase.

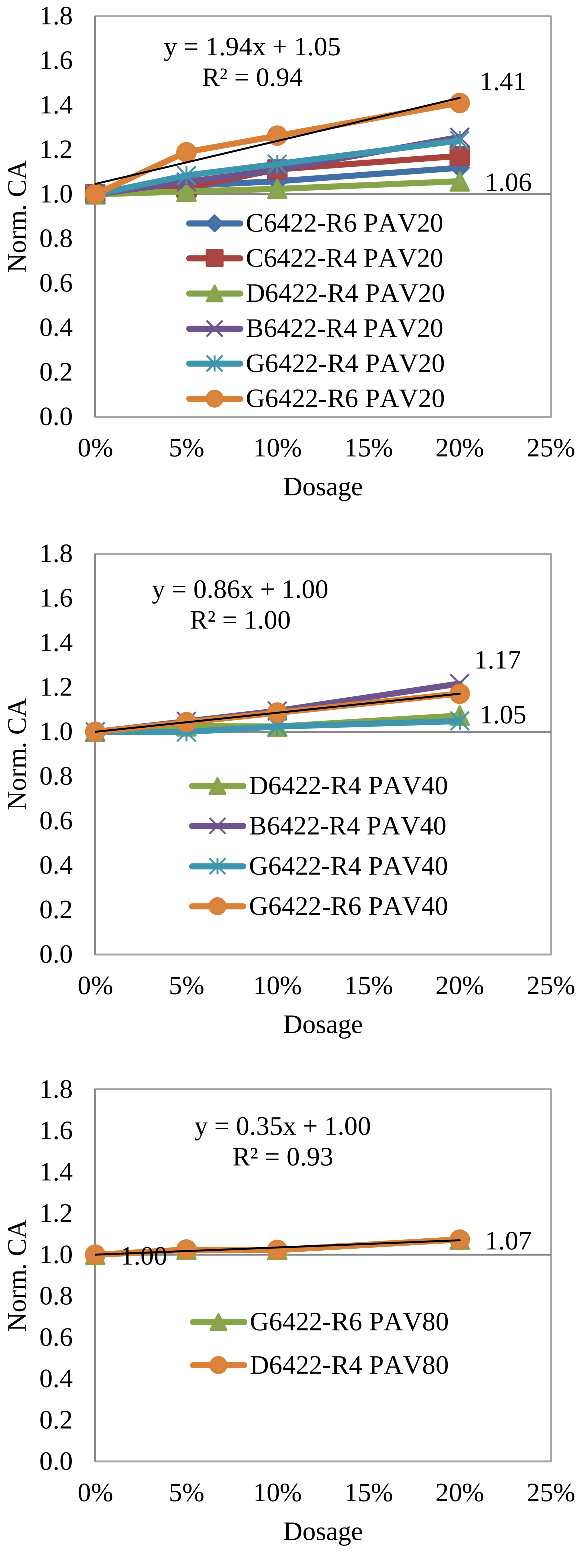
In summary, FTIR results show that binder aging properties are influenced more by (a) REOB dosage, (b) REOB source, and (c) level of aging than the source of binder. The results also show that higher REOB percentage negatively impact aging potential of binders.



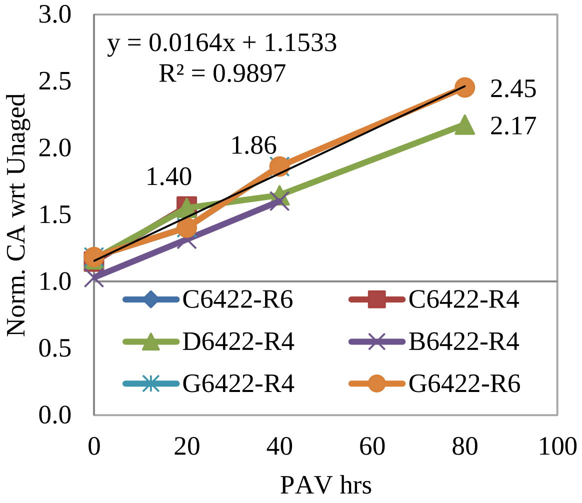
(a) Carbonyl Area

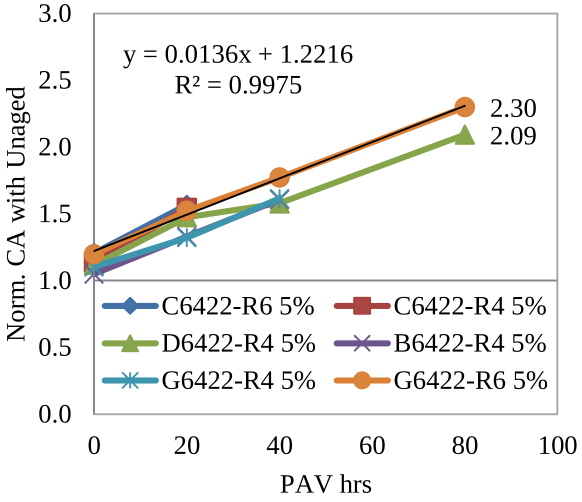

y = 2.82x + 0.99
R² = 0.99
1.55
1.30
1.10
1.15
Norm. CA
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0%
5%
10%
15%
20%
25%
Dosage
C6422-R6 Unaged
C6422-R4 Unaged
D6422-R4 Unaged
B6422-R4 Unaged
G6422-R4 Unaged
G6422-R6 Unaged

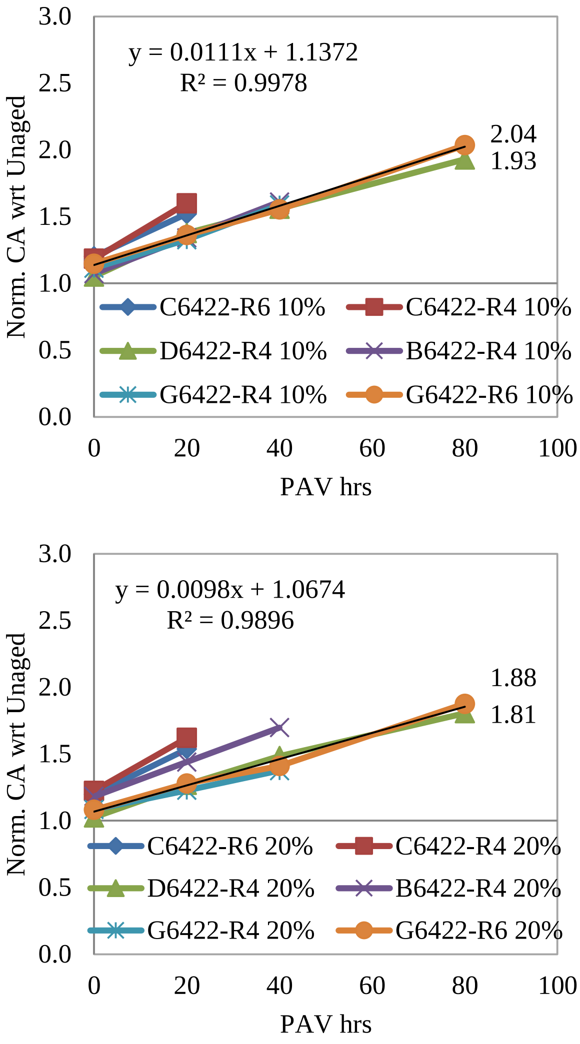

y = 2.10x + 1.01
R² = 0.98
1.41
1.14
Norm. CA
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0%
5%
10%
15%
20%
25%
Dosage
C6422-R6 RTFO
C6422-R4 RTFO
D6422-R4 RTFO
B6422-R4 RTFO
G6422-R4 RTFO
G6422-R6 RTFO



(b) Normalized Carbonyl Area for Unmodified Binders


y = 0.0164x + 1.1533
R² = 0.9897
2.45
2.17
1.86
1.40
C6422-R6
C6422-R4
D6422-R4
B6422-R4
G6422-R4
G6422-R6
Norm. CA wrt Unaged
PAV hrs
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100


y = 0.0136x + 1.2216
R² = 0.9975
2.30
2.09
C6422-R6 5%
C6422-R4 5%
D6422-R4 5%
B6422-R4 5%
G6422-R4 5%
G6422-R6 5%
Norm. CA with Unaged
PAV hrs
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
20
40
60
80
100



(c) Normalized Carbonyl Area for Unaged Binders

Figure 40. Carbonyl Area in Unmodified and REOB-Modified Binders.

IMPACT OF REOB ON BINDER SARA COMPOSITION

Binder chemical compositions are often classified as the separation of SARA. Researchers investigated the effect of REOB on the concentration of asphaltenes, saturates, resins, and aromatics. In general, high concentration of extremely polar compounds is not good for binders to perform well in the field. Asphalt colloidal model hypothesizes that solid particles of asphaltenes are dispersed in a liquid medium made of saturates and aromatics; resins aid in dispersing asphaltenes well uniformly (Swanson 1942; Park and Ali Mansoori 1988; Asomaning 2003; Ashoori et al. 2017). For this study, SARA fraction separation was carried out on Iatroscan MK-6s instrument using the thin layer chromatography and flame ionization techniques (IP 469:2001 2006).

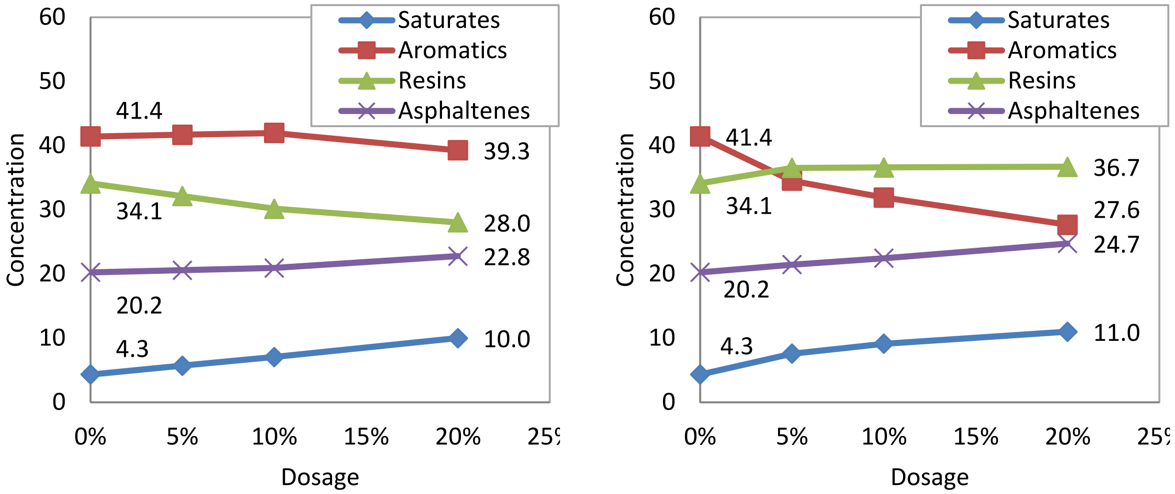
Figure 41(a) presents the concentrations of asphaltenes, saturates, resins and aromatics in unaged and PAV-aged blends. The figure shows that addition of REOB increased the concentrations of saturates and asphaltenes while decreased the concentrations of aromatics and resins. The figure also displays that these relationships stay similar in both unaged and PAV-aged binders. These influences are consistent with the results of a recent study conducted by the Western Research Institute (Planche et al. 2015). This increase in the concentration of insoluble compounds (i.e., asphaltenes) and the decrease in the concentration of compounds (i.e., resins) required to disperse asphaltenes in saturates and aromatics suggest that REOB may lead to instability in the binders. The figure also shows that the concentrations of SARA fractions changes with the change in the source and the dosage of binders and REOB as well as on the level of aging.

To further interpret the SARA data, the concentrations of SARA fractions in modified or aged binders were normalized for the concentrations of SARA fractions in unmodified or unaged binders as shown in Figure 41(b-c).

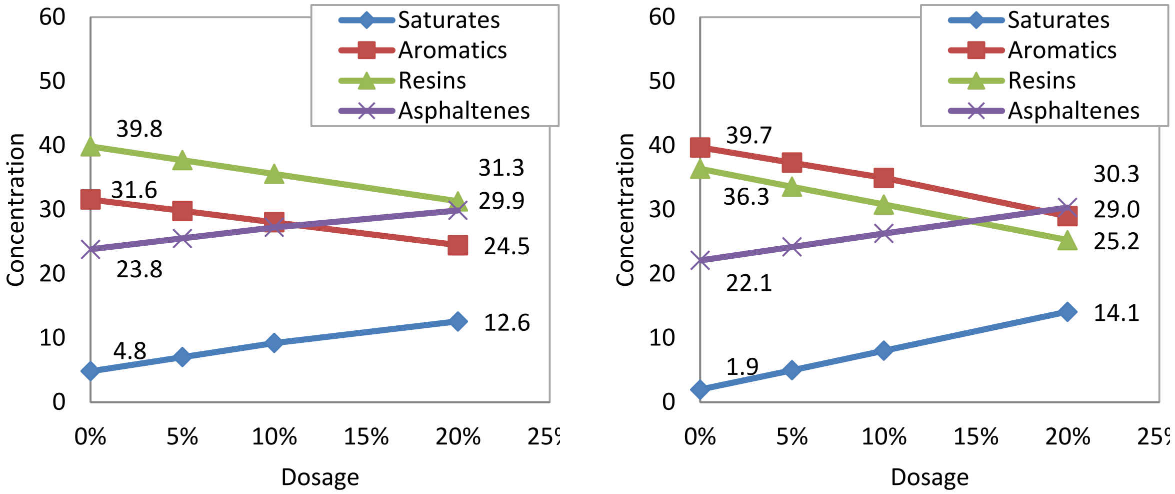
Figure 41(b) presents the normalized concentrations of SARA fractions in the modified binders for the concentrations of SARA fractions in the unmodified binders. The figure clearly shows that the change in the concentrations of asphaltenes, saturates, aromatics, and resins were not the same for different sources and dosages of binders and REOB. The figure also demonstrates that the change in saturates was higher than the change of other compounds in both unaged and aged binders, implying compounds other than saturates were not significantly impacted by progression of aging. Similarly, the figure also shows that the change in saturates were higher in aged binders than in unaged binders implying aging of REOB-modified binders drastically changes chemical composition.

Figure 41(c) presents the normalized concentration of SARA fractions in the PAV-aged binders for the concentration of SARA fractions in the unaged binders. The figure clearly shows that, in most cases, aging mostly increased the normalized values of saturates and asphaltenes but mostly decreased the normalized values of resins and aromatics. Additionally, the figure also reconfirms the dependence of this change on the source and the dosage of binder and REOB.

In summary, these figures show that REOB source and dosage have influence on chemical composition/properties of binders and that these influences are further affected by the source of binder and level of aging.

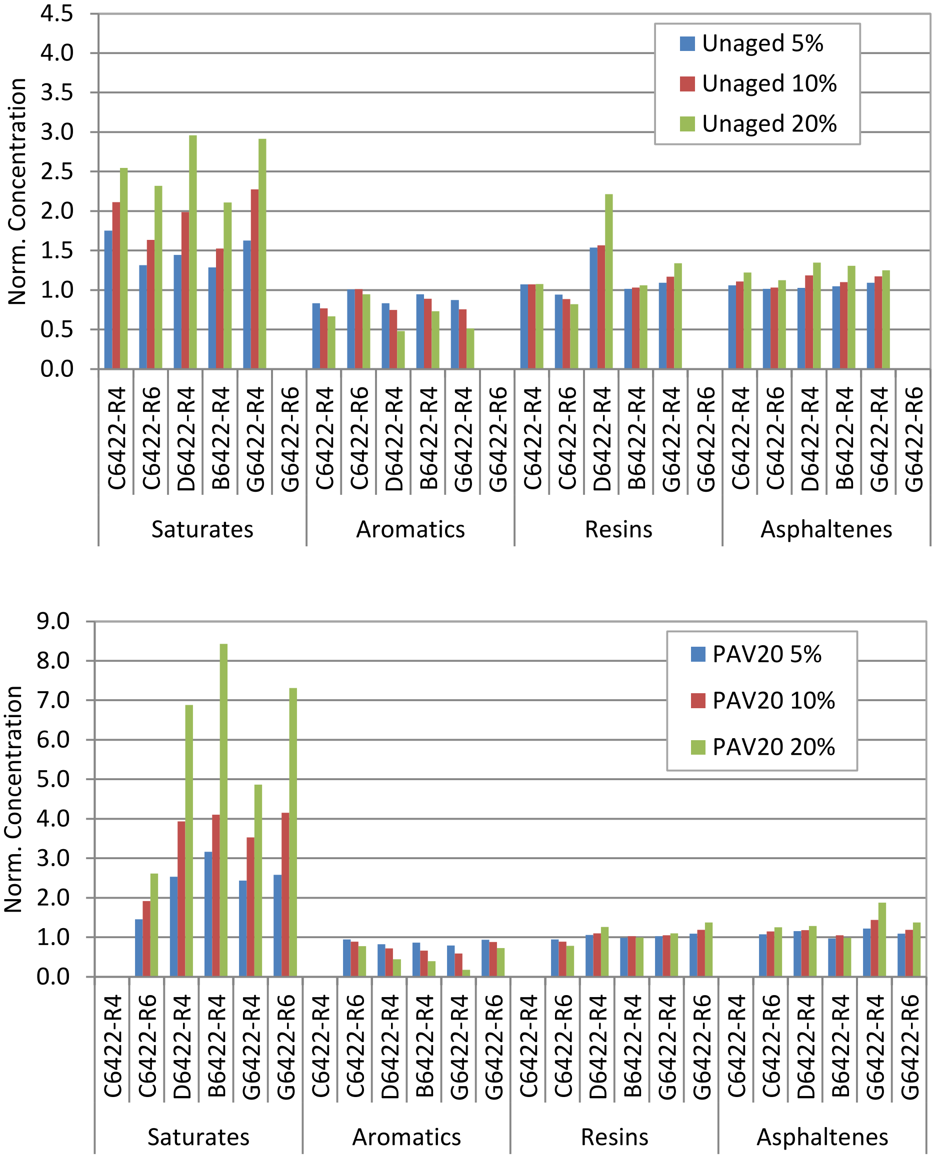


Unaged C6422-R6 **Unaged C6422-R4**

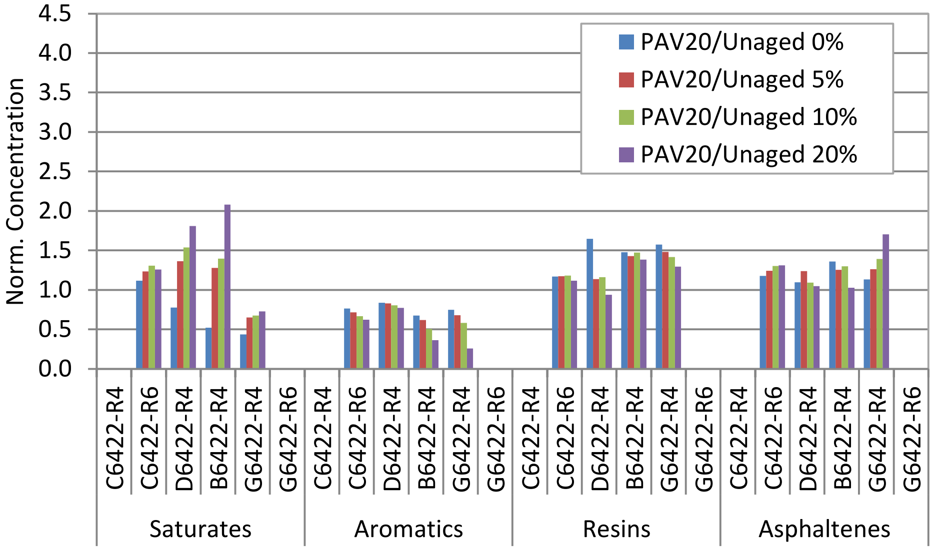


PAV20-Aged C6422-R6 **PAV20 Aged G6422-R6**

(a) SARA Concentration in Unaged and Aged Binders



(b) Normalized SARA Concentrations for Unmodified Binder



(c) Normalized SARA Concentrations for Unaged Binder

Figure 41. SARA Fractions in Unmodified and REOB-Modified Binders.

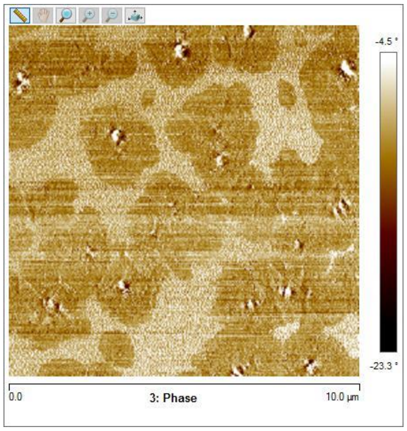
IMPACT OF REOB ON BINDER MICROSTRUCTURES

In addition to the rheological and chemical tests, researchers also employed the advance AFM imaging technology to look at the microstructure of asphalt binders modified with REOB. Previous studies have reported that base binders are populated with bee-like structures (Nahar et al. 2013; Allen et al. 2014; Jahangir et al. 2015) and that these structures change their shape with application of load (Jahangir et al. 2015). It has been also reported that the addition of REOB also changes the microstructure of asphalt binders (Planche et al. 2015). Researchers employed Bruker Multimode 8.0 AFM instrument to investigate the impact of REOB on microstructure change of D64-22 binder under different aging conditions.

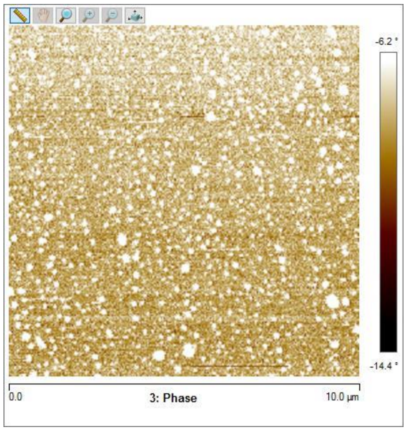
Figure 42(a) presents the topographical images of unaged, RTFO-aged, and PAV-aged samples of D6422 base binder as obtained from their AFM tests. The images show that microstructures of binder contain a number of distinct bee-like structures scattered surrounded by some patches, and that the number and the size of these structures increase with aging. Previous studies have mentioned that the number of bee-structures in AFM images of binders can be correlated with the concentrations of asphaltenes and waxes (Planche et al. 2015), which is supported by the fact that aging increases asphaltene concentration as shown by SARA tests just above.

Figure 42(b) presents the topographical images of unaged, RTFO-aged, and PAV-aged samples of D6422 binder treated with 20 percent REOB. The figure shows that the microstructure of REOB modified binders did not contain any bee-like structures. Instead, these microstructures were populated with evenly distributed tiny light-colored spots or pigmented structures. The structures decreased in number but increased in size with increased level of aging. After severe or PAV-aging, even larger and darker patches populated the images. The aforementioned previous study also mentioned that darker spots were present in AFM images of aged, REOB-modified binders, and that the number of such spots increased with aging (Planche et al. 2015).

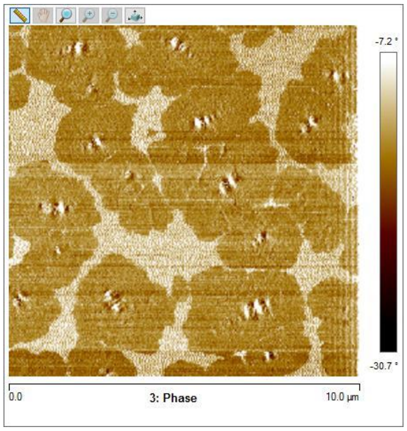
The study identified them as a separate phase that might represent either a harder or a less sticky phase. The significantly different features revealed in the microstructural images of unmodified and REOB-modified binders at all three selected level of aging conditions suggest that REOB affects binder surface structure at all stages of their lifecycles, and this effect potentially plays important role in performance.



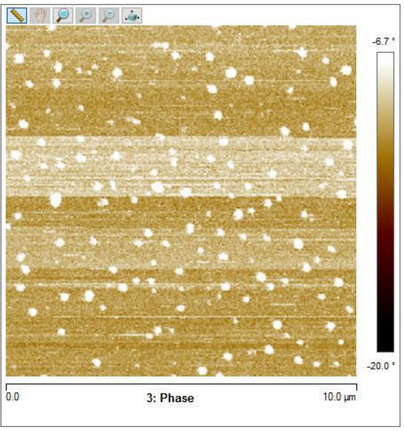
Unaged



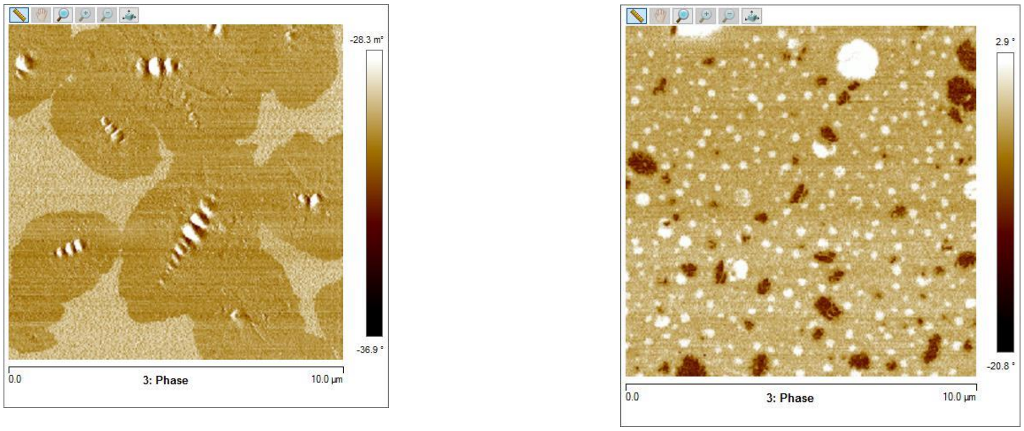
Unaged



RTFO-Aged



RTFO-Aged



PAV-Aged **PAV-Aged**

(a) D6422 Binder **(b) D6422 Binder + 20%R4**

Figure 42. AFM Images of Unmodified and REOB-Modified Binders.

PERFORMANCE EVALUATION OF THE SAME PG BINDERS MODIFIED WITH REOB AND OTHERS

Transportation agencies or their assigned contractors purchase asphalt binders for pavement construction based on specified PG. Binder suppliers can produce binders that meet the purchase specifications (i.e., PG) by modifying the stiffer base binders with different amount of in-house products such as REOB, PPAs, and other additives. The foregoing sections showed that REOB and PPA influence asphalt properties including PG and others. To further evaluate the influence of REOB on binder properties, the following section evaluates the performance of asphalt binders having the same PG but modified with REOB and other additives.

Laboratory Modified PG58-28 Binders

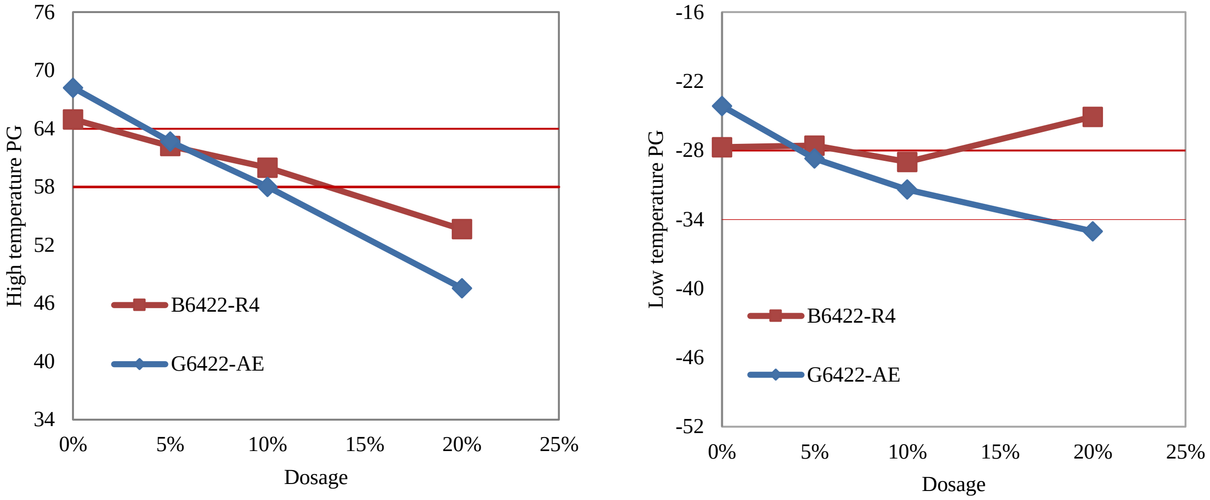
A total of seven PG58-28 binders, as listed below, were made in the laboratory through adding different additives (REOB, PPA, RAP binder, and AE) to the two base binders, PG64-22 and PG58-28 binders (i.e., B6422, G6422, and G5828):

- Straight PG58-28 binder without any modifications.
- Straight PG58-28 modified with REOB to get a PG58-28.
- Straight PG58-28 + extracted RAP binder + high amount of REOB to get a PG58-28.
- Straight PG58-28 + low amount of PPA + low amount of REOB to get a PG58-28.
- Straight PG58-28 + high amount of PPA + high amount of REOB to get a PG58-28.
- PG64-22 modified with REOB to get a PG58-28.
- PG64-22 modified with Hydrolene (i.e., an AE) to get a PG58-28.

To determine the percentage of REOB, PPA, and RAP binder required to obtain these blends that satisfy PG58-28 specification, a series of PG tests were performed. Figure 43 presents the true high and low temperature PGs of binders obtained by blending PG64-22 binder with REOB

(B6422 with R4) and AE (G6422 with AE) at four different dosage rates (0 percent, 5 percent, 10 percent, and 20 percent).

Using high temperature PG data, the minimum and the maximum dosages of REOB required to meet PG = 58 were estimated. Similarly, low temperature PG data were used to calculate the minimum and the maximum dosages of REOB required to meet PG = −28. Table 21 presents these values, along with selected dosage within these limits. The figure and table clearly show that, in comparison to REOB, a lesser amount of AE is needed to change PG from 64-22 to 58-28.



(a) High Temperature PG **(b) Low Temperature PG**

Figure 43. Correlation of High and Low Temperature PGs with Modifier Dosage.

Table 21. Different Recipes to Produce PG58-28 Binder: An Example.

Dosage	B6422-R4				G6422-AE			
	High PG	Low PG	Both	Selected	High PG	Low PG	Both	Selected
Min.	2.0%	6.5%	6.5%	10%	4.0%	4.2%	4.2%	5%
Max.	12.6%	12.6%	12.6%		9.8%	17.2%	17.2%	

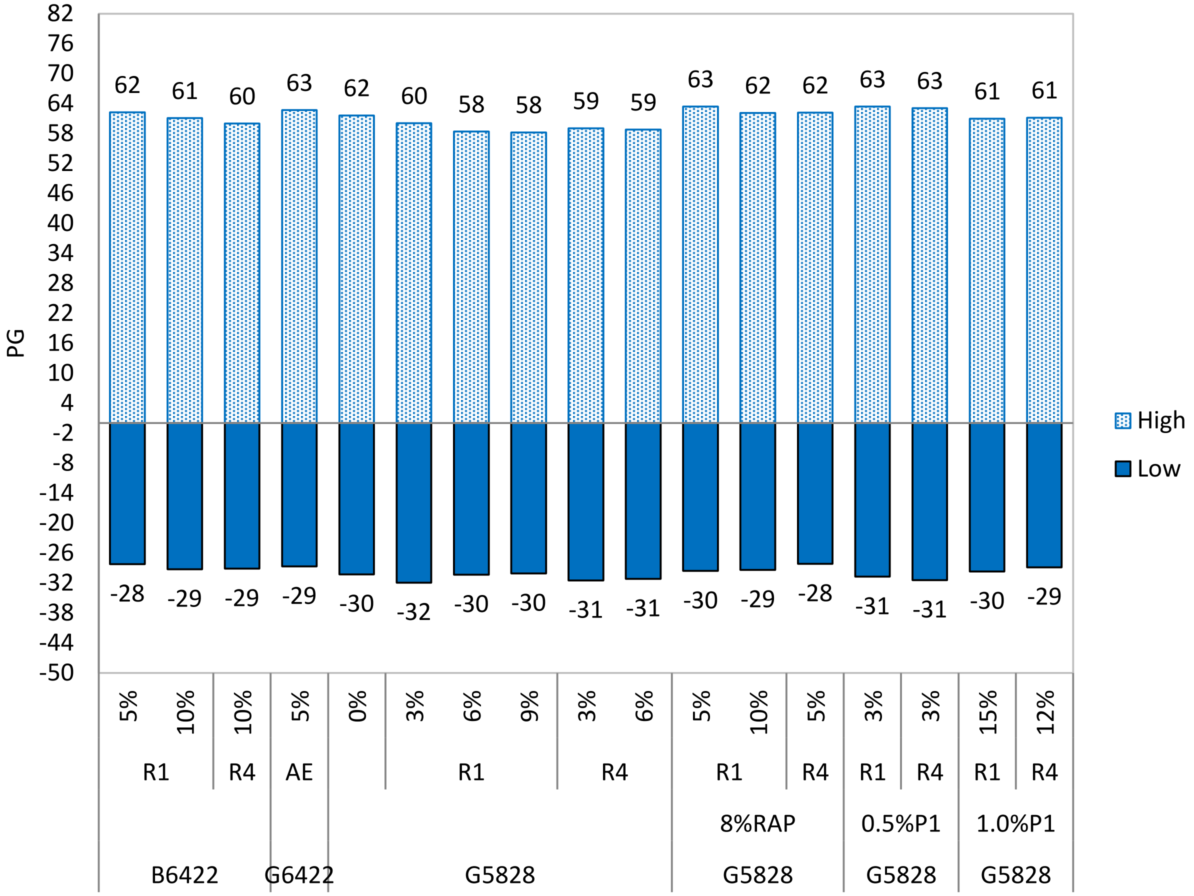
The same method was employed to estimate dosages of each modifier (i.e., REOB, PPA, and RAP-extracted binder) required to change the PG of the remaining combinations to PG58-28. Table 22 presents the selected dosages of modifiers used in these blends.

Table 22. Different Recipes to Produce PG58-28 Binder.

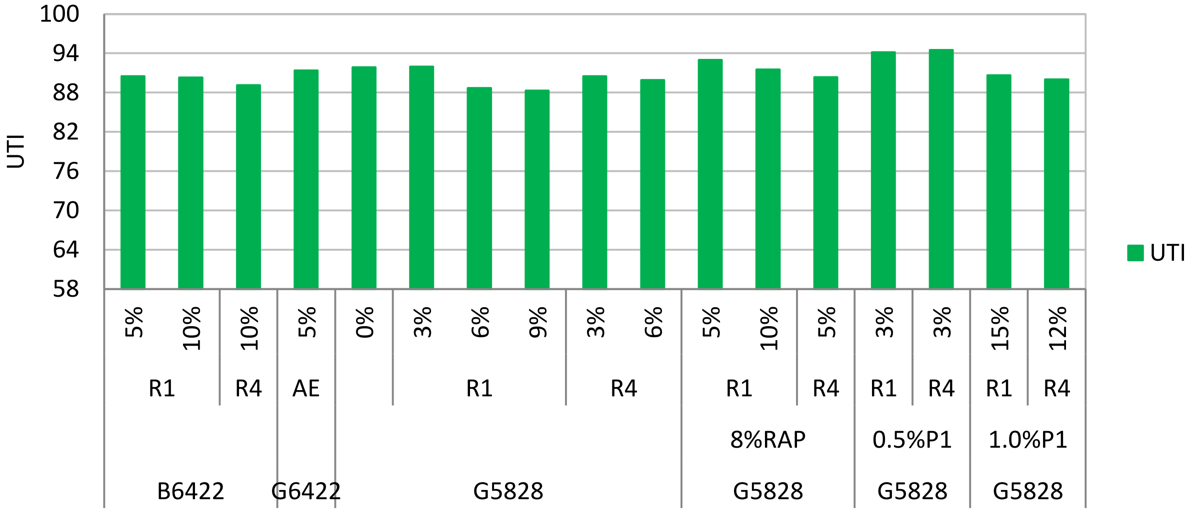
Binder	Initial PG	Modifier #1	%	Modifier #2	%
B6422	64-22	R1	5%	-	-
			10%		
		R4	10%		
G6422		AE	5%	-	-
G5828	58-58	None	-	-	-
		R1	3%	-	-
			6%		
			9%		
		R4	3%		
			6%		
		R1	5%	RAP	8.0%
			10%		
		R4	5%		
		R2	3%	P1	0.5%
		R4	3%		
		R1	15%		1.0%
		R4	12%		

Figure 44(a) presents the high and the low temperature PGs of selected blends, and Figure 44(b) presents the useful temperature interval (UTI) (the gap between high and low temperature PGs) of these blends. Figure 45 presents the difference in m-value and stiffness-based critical low temperature grades of these blends, ΔTc.

Figure 44(a) specifically shows that selected blends successfully met PG58-28 and that there was minimal difference in their final true grades. Figure 44(b) shows that the temperature range over which these binders would perform well based on their PG differed only slightly. However, Figure 45 shows that there is significant difference between ΔTc values of these blends, suggesting different cracking potential at low temperature conditions. The figure also shows that ΔTc of PG58-28 binders prepared by blending PG58-28 and PG64-22 binders with REOB, PPA, and RAP binder ranged from −5°C to −14°C while ΔTc value of unmodified binder was only −2°C. As such, pavements constructed using these modified binders would likely accumulate more distresses than the pavements constructed with unmodified PG58-28 binder based on the work done by Bennert et al. (2016). To synopsize, the figures provide strong evidence that PG alone might not guarantee good performance of binders and that REOB-, PPA-, and RAP-extracted binder makes binders more prone to cracking, especially at low temperature. The figures also show that this effect depends on the source and the dosage of REOB, and the source and the PG of binders as proven in foregoing section.



(a) High and Low Temperature PGs



(b) UTI

Figure 44. PG Test Results of Selected Blends.

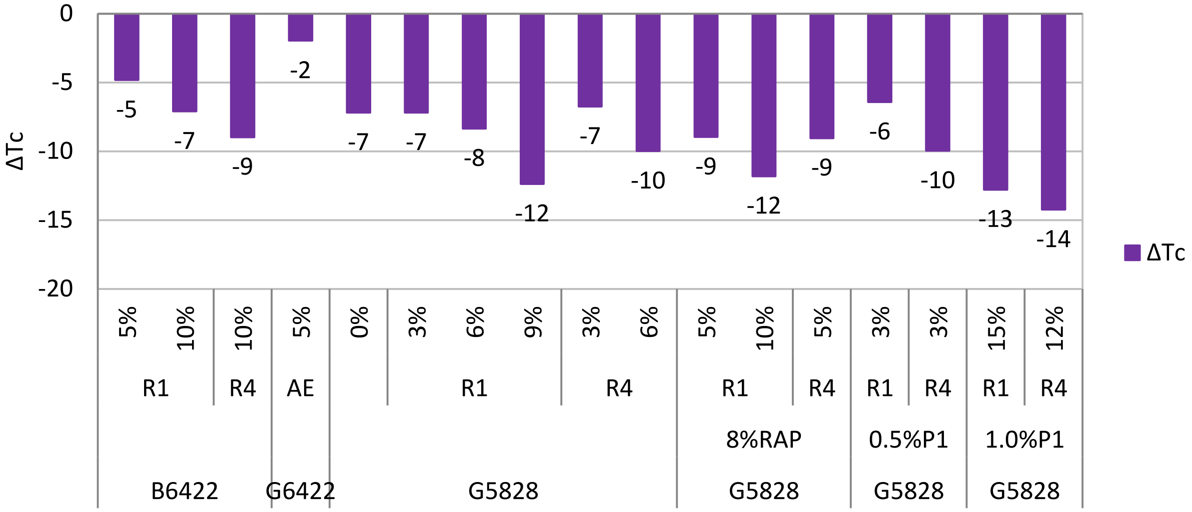
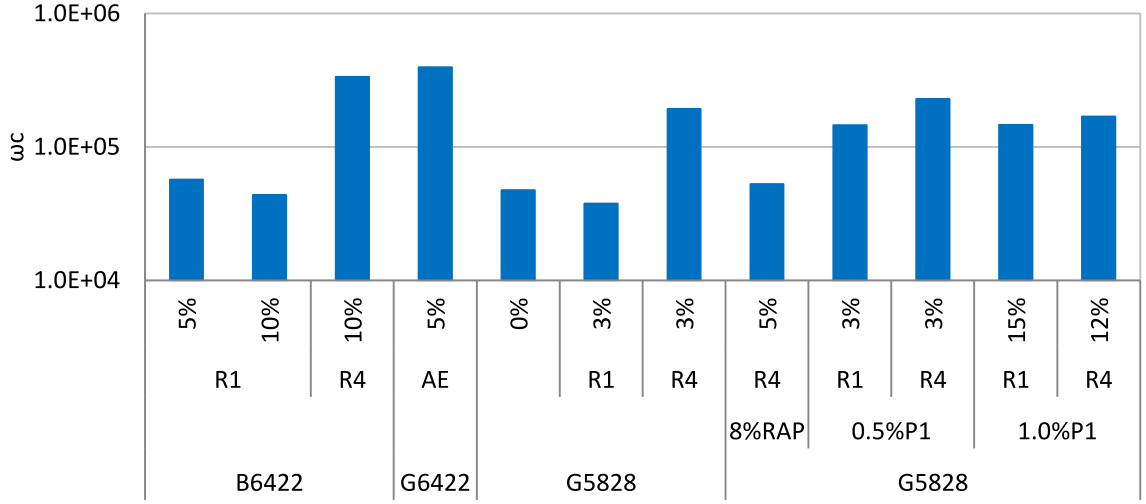


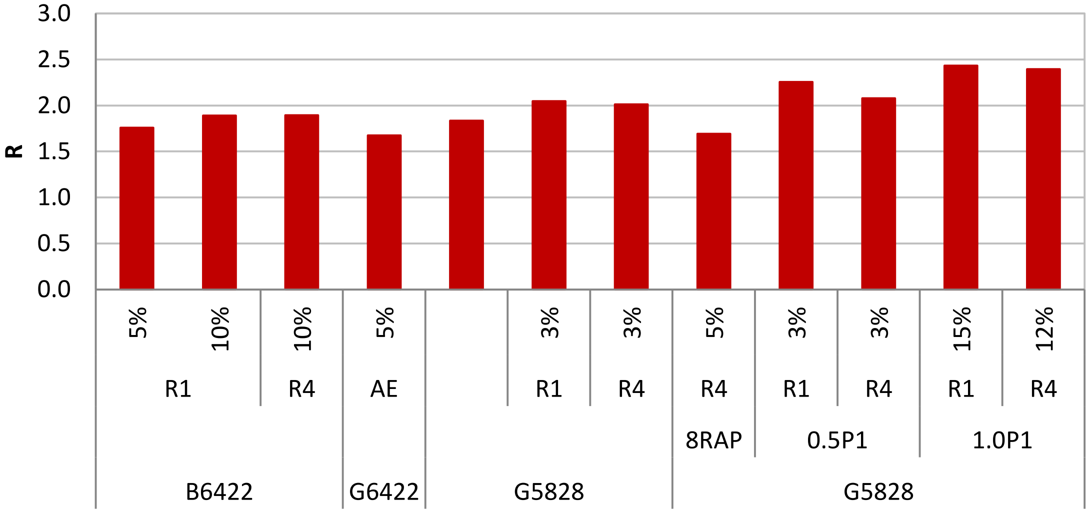
Figure 45. ΔTc Values of Selected Blends.

Properties of Selected Binder Combinations

Figure 46(a) and Figure 46(b) present the crossover frequency and rheological index of PG58-28 binders prepared by blending PG64-22 and PG58-28 binders with different REOB-, PPA-, and RAP-extracted binder at different dosages. The figure shows that, in general, PG58-28 binders obtained from REOB/PPA/RAP-modified binders have higher crossover frequency and higher rheological index than the unmodified PG58-28 binder. But the one with AE has higher crossover frequency but lower rheological index than the base PG58-28 binder. As described above, the higher crossover frequency refers to comparatively softer material and the higher rheological index refers to materials with slower transition from elastic-to-viscous state. As such, despite having same PG, PG58-28 binders obtained from AE-modified binders are also softer but have faster transition from elastic-to-viscous state than the unmodified PG58-28 binder, making such binders more compliant to loading frequency and temperature change. Similarly, PG58-28 binders obtained from REOB-modifier binders are softer but have faster transition from elastic-to-viscous state than the unmodified PG58-28, making such binders less compliant to loading frequency and temperature change, a possible cause of more distresses in pavements constructed with REOB-modified binders. Also evident from these figures is the dependence of these effects on the source and PGs of binders, and sources and dosages of modifiers.



(a) Crossover Frequency: ωc



(a) Rheological Index: R

Figure 46. Frequency Sweep Test Results of Selected Blends.

SUMMARY

This chapter evaluated the effects of different sources and dosages of REOB on properties of binders obtained from different sources. Based on the results presented in the foregoing sections, the following conclusions could be drawn:

1. **High PG:** REOB, AE, and BR reduce the high temperature PG of base binder, confirming their softening effect. However, the degree of this effect totally depends on modifier type, source, and dosage. In general, AE is more effective than REOB, but less effective than the selected BR. The source of REOB has more pronounced effect on high temperature PG of base binder than the source of binder itself. REOB and PPA have quite opposite effect on high temperature PG of binders. REOB reduces the high temperature

PG while PPA increases its value, confirming the role of PPA as a stiffening agent while that if REOB acts as a softening agent. The same amount of PPA is considerably more effective in changing high temperature PG than the same amount of REOB. In other words, a much smaller amount of PPA, when compared to REOB, is required for changing the high temperature PG of base binder.

2. **Low PG:** Low temperature PG of binders is more influenced by binder source, REOB source, and REOB dosage based on stiffness criterion than relaxation slope criterion. In other words, REOB are more effective in degrading stiffness properties of binders than in enhancing the flow (or viscous) properties of binder. AE and BR were more effective than any REOB in changing low temperature PG. REOB and PPA have quite different effect on $\mathrm{T_{c-m}}$ and $\mathrm{T_{c-S}}$. The same amount of PPA is more effective in changing low temperature PG than the same amount of REOB.
3. **Delta $\mathbf{\Delta T_c}$:** ΔT_c becomes more negative with an increase in REOB or PPA dosage, irrespective of the source of binder, REOB, and PPA. However, the trend reverses when binders are modified with AE or BR instead. This suggests the use of significantly high percentage of REOB or PPA can make binders less capable of relaxing stress at low temperature, and thereby more prone to cracking. Inversely, binders modified with AE or BRs make binders more capable of relaxing stress at low temperature, and thereby less prone to cracking.
4. **Rheology**: REOB and aging have completely opposite effects on crossover frequency or stiffness (i.e., softening vs., hardening) but quite similar effects on rheological index or elastic-to-steady state transition (i.e., make it slower). REOB, AE, and BR have similar effects on crossover frequency or stiffness (i.e., softening effect) but have opposite effects on rheological index or elastic-to-steady state transition (i.e., make it slower vs. faster). In summary, REOB, AE, and BR all soften but aging hardens the binders. In terms of letting binders reach steady (viscous) state from elastic state, aging and REOB are more effective than AE and BR.
5. **Chemical Aging:** Carbonyl area increases with aging for any given binder source, REOB source, and REOB dosage. Of particular interest is the fact that carbonyl area in unmodified binder after certain duration of aging is equivalent to the carbonyl area in binder unaged binder modifier with a certain amount of REOB. This suggests that aging and addition of REOB might have negative effect on ability of binders to further age. Also, after certain level of aging, there is minimal difference in normalized carbonyl areas of binders blended with higher and lower dosages of REOB, suggesting binders modified with higher dosages of REOB can longer age due to high concentration of carbonyl area already in them. Carbonyl area increased with elevated level of aging. However, the figure also shows that the rate of increase reduced with higher dosage of REOB. Additionally, the figure also shows sources of binders and REOB both affect this increase.
6. **SARA**: REOB increases the concentrations of saturates and asphaltenes while decreased the concentrations of aromatics and resins. These relationships stay similar in both unaged and PAV-aged binders. This increase in the concentration of insoluble compounds (i.e., asphaltenes) and the decrease in the concentration of compounds (i.e., resins) required to disperse asphaltenes in saturates and aromatics suggest that there might be some phase instability issues in such blends. Similarly, the change in the concentrations of asphaltenes, saturates, aromatics, and resins was not the same for

different sources and dosages of binders and REOB. The change in saturates is higher than the change of other compounds in both unaged and aged binders, that is the compounds other than saturates are not significantly impacted by aging.

7. **Microstructure**: The microstructures of binder contain a number of distinct bee-like structures scattered surrounded by some patches, and that the number and the size of these structures increase with aging. However, the microstructures of REOB modified binders do not contain these structures. Instead, these microstructures are populated with evenly distributed tiny light-colored spots or pigmented structures. The structures decrease in number but increase in size with increased level of aging. This suggests that REOB affects binder surface structure at all stages of their lifecycle.
8. **Overall**: This part of the study suggests that (a) PG specification alone might not guarantee well performing binders, (b) REOB effect rheological, chemical, and structural properties of binders, and (c) these effects depend on the source and the dosage of both the REOB and the binders, and presence of other modifiers such as RAP-extracted binders and PPA, etc.

CHAPTER 6: IMPACT OF REOB ON ASPHALT MIX PROPERTIES

Asphalt binder plays important role in asphalt mixture properties, but asphalt binder alone cannot determine how asphalt mixture performs, because around 95 percent asphalt mixtures are composed of aggregates. Thus, it is critical to evaluate how REOB impacts performance of asphalt mixtures, which is the focus of this chapter.

LABORATORY EXPERIMENTAL DESIGN

Material Selection

One PG64-22 asphalt binder (G6422) and two REOB (R1 and R4) were selected for this study. These REOB, R1 and R4, are most often used to modify asphalt binder properties. For each REOB modification, the virgin PG64-22 binder was modified by adding three dosages of REOB: 0, 5, and 10 percent. Thus, a total of five asphalt binders were produced: (1) virgin PG64-22, (2) PG64-22/5%R1, (3) PG64-22/10%R1, (4) PG64-22/5%R2, and (5) PG64-22/10%R2.

Two dense-graded mix types were employed in this study to evaluate the influence of REOB on asphalt mixture properties; one is a virgin mix and the other being a 17%RAP/3%RAS mix. Figure 47 displays the aggregate gradations of asphalt mixes used in this study. For each mix type, five mixtures were produced with those five REOB modified binders in the laboratory. The optimum asphalt content for every mix was kept same: 5.4 percent. For the 17%RAP/3%RAS mixes, recycled binder from the RAP/RAS was 27.8 percent the total binder.

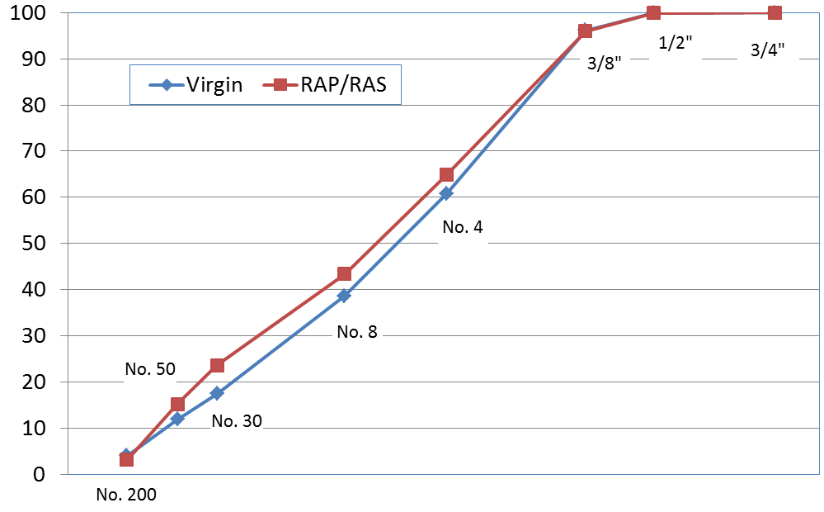


Figure 47. Gradations of Dense-Graded Asphalt Mixtures for REOB Study.

Samples Preparation and Laboratory Tests

Both rutting and cracking resistance of asphalt mixtures were evaluated in this study. The HWTT was employed to evaluate rutting potential; Texas OT, InDirect tEnsion AsphaLt Cracking Test (IDEAL-CT), and the Illinois version of Semi-Circular Bending (SCB) tests were used for assessing cracking resistance of REOB mixes. Detailed information for each test is described below.

Hamburg Wheel Tracking Test

Two 150 mm in diameter and 62 mm high samples for the rutting test were compacted to 7±0.5 percent air voids after the loose mixes were aged in an oven at the compaction temperature of 275°F. The HWTT (Figure 48) was performed following TxDOT standard test procedure Tex-242-F. One set of HWTT samples was run in a water bath set to 122°F with 158 lb vertical wheel load at a speed of 50±2 load passes per minute. The rut depth at specific load passes is reported, depending on the asphalt binder PG grade.

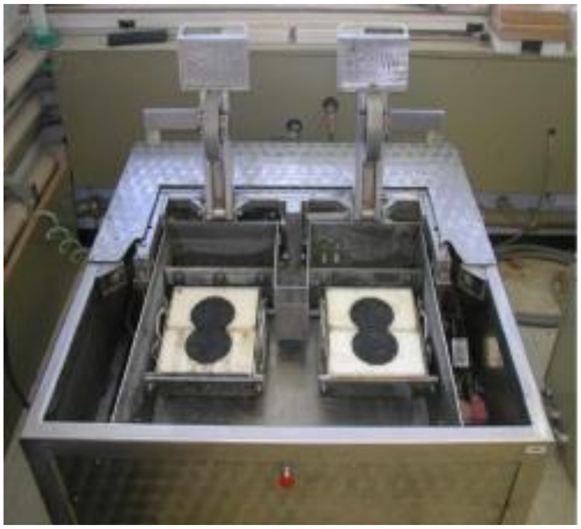


Figure 48. HWTT Used in This Study.

Texas Overlay Test

The OT (Zhou and Scullion 2005) samples were molded after aging the loose mixes in four hours at 275°F. Compared to the HWTT samples, four hours aging rather than two hours were used for cracking test samples. The reason for increasing two more hours aging is that cracking often occurs at a much later time and longer aging simulates field condition much better. A total of five replicates were molded for each mix. These molded samples were then cut into standard OT specimens: 150 mm long by 75 mm wide and 38 mm high. The air voids for each specimen was controlled within 7±0.5 percent after cutting. The OT (Figure 49) was performed following Tex-248-F. It was run at 77°F with a maximum opening displacement of 0.025 inch and a triangle loading wave form of 10 second per cycle. The number of cycles to failure was reported at the end of the test. Five replicates of OT samples were tested and the average value of OT cycles was used to evaluate the cracking resistance of each mix.

Figure 49. OT Used in This Study.

IDEAL-CT

The IDEAL-CT (Figure 50) was recently developed at TTI under the National Cooperative Highway Research Program-IDEA Project 195 (Zhou et al. 2017). Similar to OT samples, the 150 mm in diameter and 62 mm high samples were compacted to 7±0.5 percent air voids after 4 hours aging at 275°F in an oven. A total of five specimens were molded for each mix. The IDEAL-CT test was performed at 77°F, and a monotonic load was applied vertically to the specimen at a constant displacement loading rate of 50 mm/min. The load and load line displacement were recorded during the whole test period. A cracking index, $\mathrm{CT}_{\mathrm{index}}$, was calculated considering the combined effect of fracture energy, cracking propagation rate, and deformation tolerance. The larger the $\mathrm{CT}_{\mathrm{index}}$ is, the better the cracking resistance of asphalt mix. One of the main features of the IDEAL-CT is simple sample preparation: no cutting, gluing, instrumenting, notching, or drilling holes.

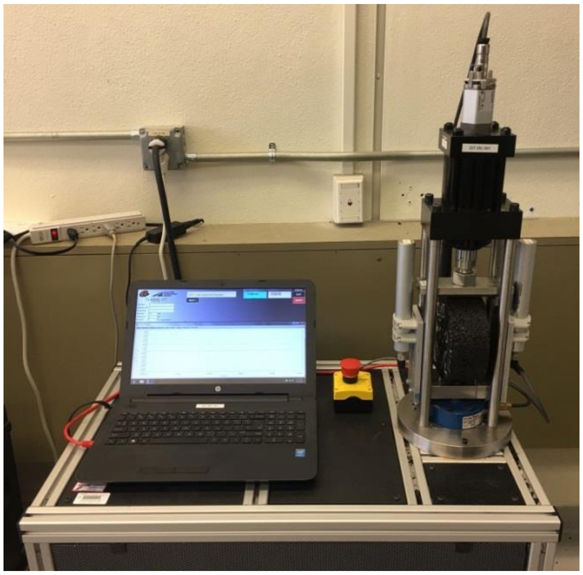


Figure 50. IDEAL-CT Used in This Study.

Illinois SCB Test

The Illinois SCB test was developed by Illinois Center for Transportation (Al-Qadi et al. 2015) to evaluate cracking potential of asphalt mixtures. The sample preparation includes four steps:

- Step 1: Compact specimens with the size of 150 mm in diameter and 61 mm height after 4 hours aging at 275°F in an oven.
- Step 2: Trim the top and bottom of the specimens to be 50 mm thick.
- Step 3: Cut the specimens into half.
- Step 4: Make a 15 mm deep and 1.5 mm wide notch on the semi-circular specimens.

Similar to the IDEAL-CT, the Illinois SCB test (Figure 51) was conducted at 77°F. During the test, a monotonic loading was applied along the vertical radius of the specimen with a constant displacement rate of 50 mm/min. A flexible index, FI, was calculated considering the combined effect of fracture energy and cracking propagation rate. The larger the FI value is, the better the cracking resistance.

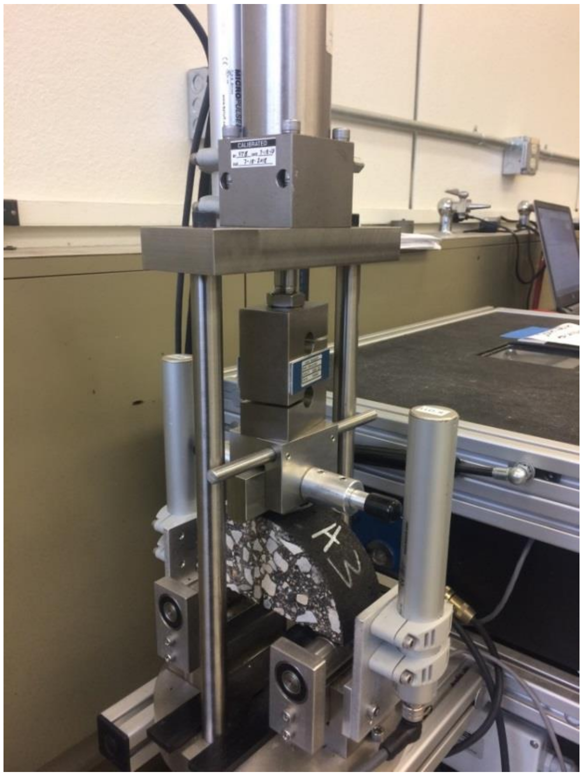


Figure 51. Illinois SCB Test.

LABORATORY TEST RESULTS AND ANALYSES

For virgin mixes with two types of REOB and three levels of REOB contents, the HWTT and three cracking test results are shown in Figure 52 through Figure 55. It can be seen from Figure 52, the increase in REOB content, as expected, reduced rutting resistance of asphalt mixes, since REOB softens the binder as discussed in Chapter 4. However, as long as its content is below

5 percent, the mixes with REOB still pass the HWTT requirement: 12.5 mm maximum rut depth at 10000 passes. Thus, from the rutting perspective, the current maximum allowable REOB content is 5 percent and should be kept the same. Regarding cracking resistance, OT results (Figure 53) indicate that REOB had no negative effect at 5 percent, but the OT cycles started to drop at 10 percent REOB. Similar observation is seen from FI data shown in Figure 54. Adding 10 percent REOB to the binder had negative influence on cracking resistance of the asphalt mix with R4, although it seems no influence on the asphalt mixes with R1. Different from OT and Illinois SCB tests, IDEAL-CT (Figure 55) showed that the REOB mixes had smaller $\mathrm{CT_{Index}}$, and the more REOB was added, the smaller became the $\mathrm{CT_{Index}}$ and the poorer became the cracking resistance. Considering both rutting and cracking test data, it can be concluded for the virgin mixes that the addition of smaller amount of REOB to asphalt binders may not have significant impact on either rutting or cracking resistance. However, when REOB content is higher than 5 percent, both rutting and cracking resistances of asphalt mixes were negatively affected. Therefore, it is necessary to set up an upper limit for the use of REOB in asphalt binders. Also the current 5 percent upper limit set by TxDOT seems reasonable for virgin mixes evaluated in this study.

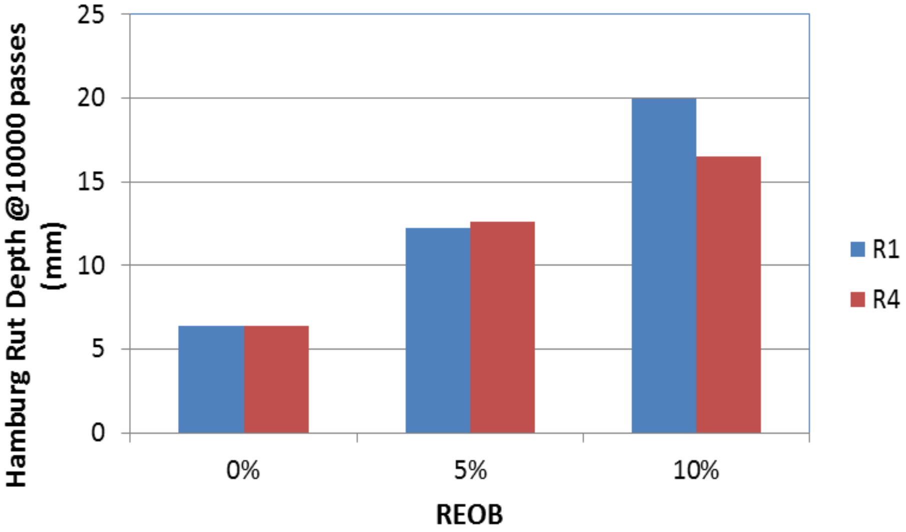


Figure 52. HWTT Test Results for Virgin Mixes.

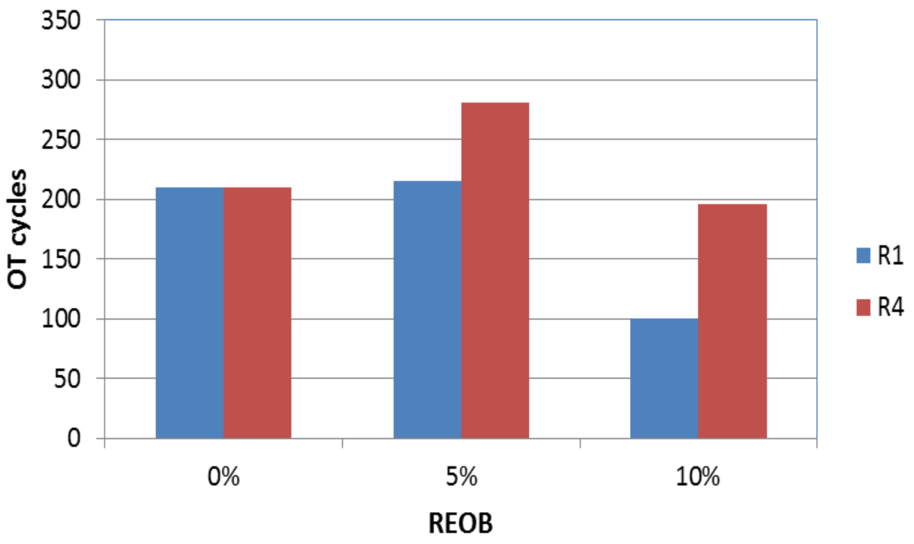


Figure 53. OT Test Results for Virgin Mixes.

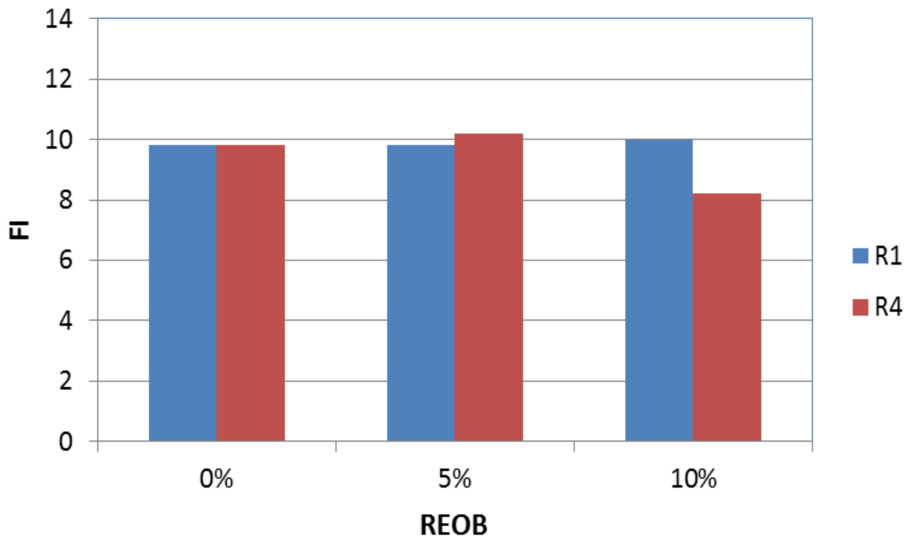


Figure 54. Illinois SCB Test Results for Virgin Mixes.

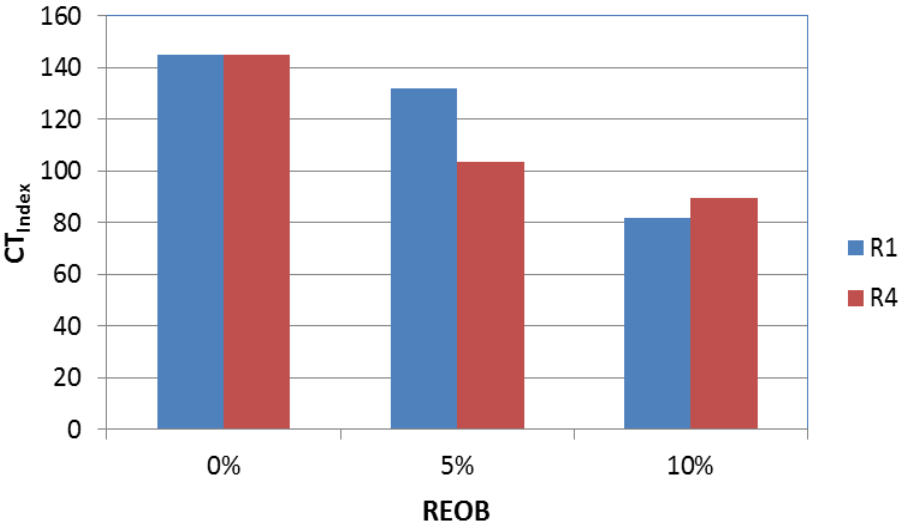


Figure 55. IDEAL-CT Results for Virgin Mixes.

Furthermore, the RAP/RAS mixes with the same two REOB and same amount of REOB as used in the virgin mixes were employed to evaluate the influence of REOB on mix properties. Figure 56 through Figure 59 display the associated rutting and cracking test results. Similar to virgin mixes, adding REOB, as shown in Figure 56, drops rutting resistance of RAP/RAS mixes. In terms of cracking resistance, REOB has very little influence on RAP/RAS mixes. This may be explained by the dominant effect of RAP/RAS on cracking resistance. The influence of REOB is overshadowed by RAP/RAS. Comparing the OT results between the virgin mix with 0 percent REOB and the RAP/RAS mix with the 0 percent REOB, OT cycles reduced from around 200 to around 15. Thus, it is very difficult to draw the conclusion that REOB has no influence on cracking resistance of RAP/RAS mixes due to the dominant effect of RAP/RAS.

In summary, the HWTT results for both virgin and RAP/RAS mixes illustrate that the addition of REOB to asphalt binder leads to poor rutting resistance of asphalt mixes, but the mixes still have acceptable rutting resistance as long as REOB content is controlled within 5 percent. For cracking resistance of asphalt mixes, it seems okay to add 5 percent REOB into asphalt binder without causing detrimental effect, but the mixes with 10 percent REOB somehow showed poor cracking resistance. Therefore, it is reasonable for TxDOT to maintain the current 5 percent upper limit for REOB in asphalt binders.

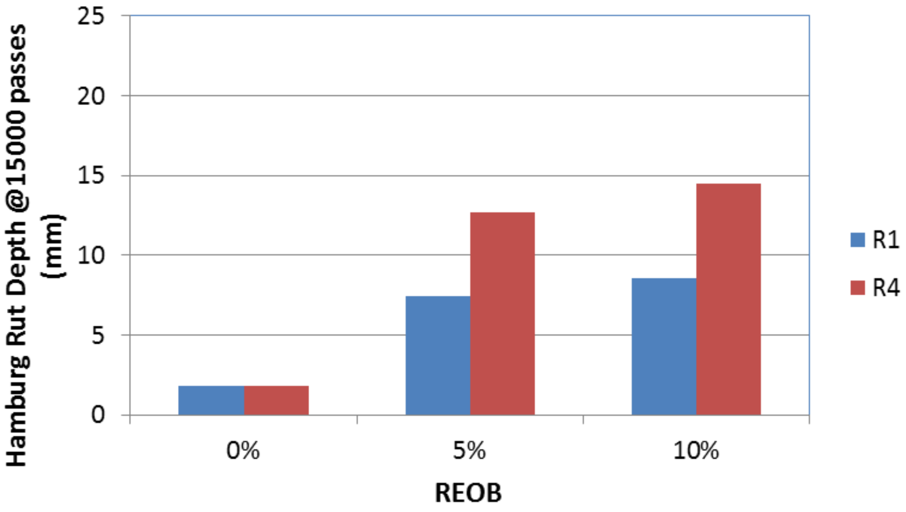


Figure 56. HWTT Test Results for RAP/RAS Mixes.

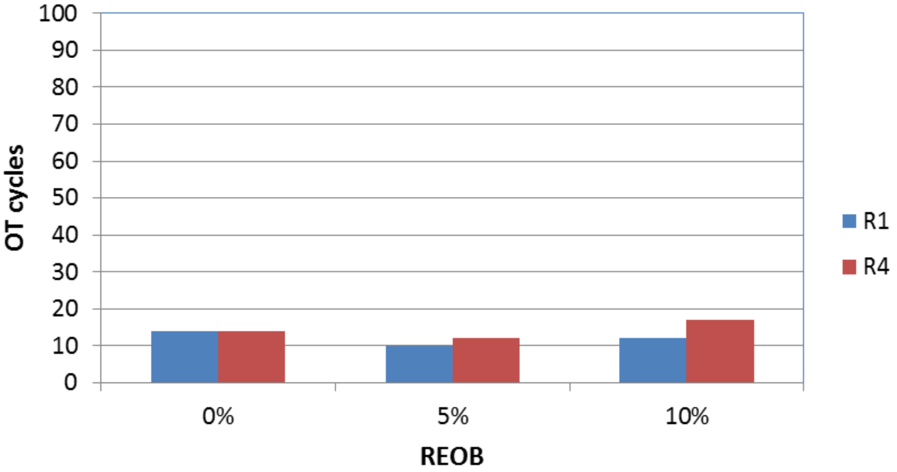


Figure 57. OT Test Results for RAP/RAS Mixes.

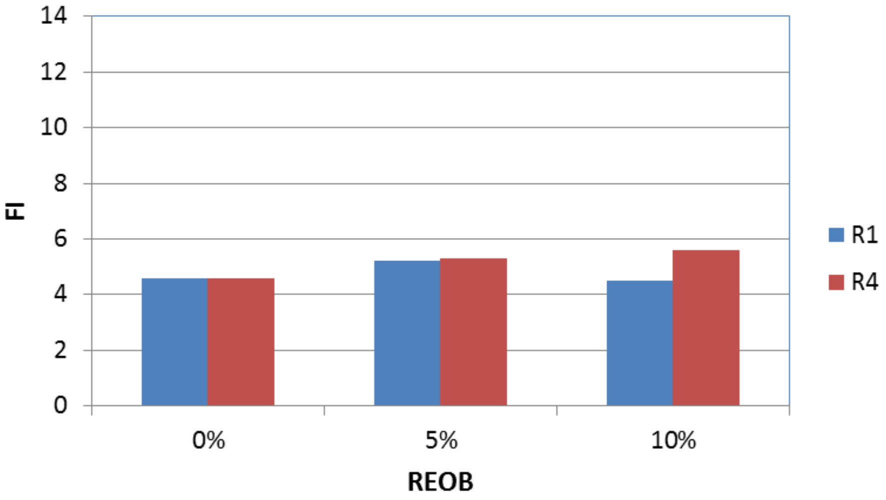


Figure 58. Illinois SCB Test Results for RAP/RAS Mixes.

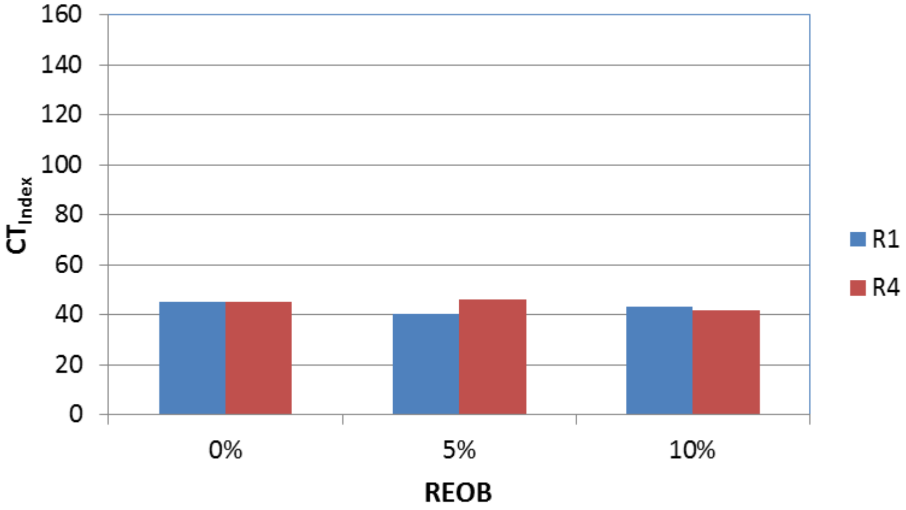


Figure 59. IDEAL-CT Results for RAP/RAS Mixes.

LABORATORY EVALUATION OF ENGINEERING PROPERTIES OF ASPHALT MIXTURES WITH PG58-28 BINDERS MADE FROM DIFFERENT MODIFICATIONS

The impact of REOB on rutting and cracking properties of asphalt mixes is discussed in last section where the same PG64-22 binder was modified with different types of REOB and various amount of REOB. The PG64-22 binder after the REOB modifications may not be PG64-22 anymore. To complement the previous section, this section investigates the rutting and cracking properties of asphalt mixes with PG58-28 binders that are modified in 10 different ways through REOB, PPA, and RAP:

- PG58-28: straight run and no modification.
- PG58-28/3%R4: PG58-28 binder plus 3 percent REOB-R4.
- PG58-28/5%R4/8%RAP: PG58-28 binder plus 5 percent REOB-R4 and 8 percent RAP binder.
- PG58-28/3%R1: PG58-28 binder plus 3 percent REOB-R1.
- PG58-28/6%R1: PG58-28 binder plus 6 percent REOB-R1.
- PG58-28/5%R1/8%RAP: PG58-28 binder plus 5 percent REOB-R1 and 8 percent RAP binder.
- PG58-28/3%R1/0.5%PPA: PG58-28 binder plus 3 percent REOB-R1 and 0.5 percent PPA.
- PG58-28/3%R4/0.5%PPA: PG58-28 binder plus 3 percent REOB-R4 and 0.5 percent PPA.
- PG58-28/15%R1/1%PPA: PG58-28 binder plus 15 percent REOB-R1 and 1 percent PPA.
- PG58-28/12%R4/1%PPA: PG58-28 binder plus 15 percent REOB-R1 and 1 percent PPA.

All these 10 asphalt binders were all graded as PG58-28 following Superpave binder specification. The same aggregates and gradation as the virgin mix in last section were used here to make asphalt mixture samples including both HWTT and OT. Again, the same HWTT and OT were performed to determine the impact of REOB on asphalt mixture properties.

Figure 60 and Figure 61 present the HWTT and OT results, respectively. Figure 60 shows that different modification techniques basically had no impact on rutting resistance. All 10 mixes had round 12.5 mm rut depths, which indicates that high temperature PG is a good indicator for rutting resistance. However, this is not the case for cracking resistance, as shown in Figure 61. Comparing with the straight run PG58-28 binder, eight out of nine modifications had poor cracking resistance in terms of OT cycles. The worst case is PG58-28 modified with 5 percent R1 and 8 percent RAP binder. Its OT cycles dropped to 121 cycles from 800 cycles of the straight run PG58-28. The data shown in Figure 61 further confirmed the previous finding: the performance of modified binders depended on the sources of REOB (PG58-28/3%R4 vs. PG58-28/3%R1). Since the same binders with the same PG grade performed differently, it is critical to test the engineering properties of the final mixtures.

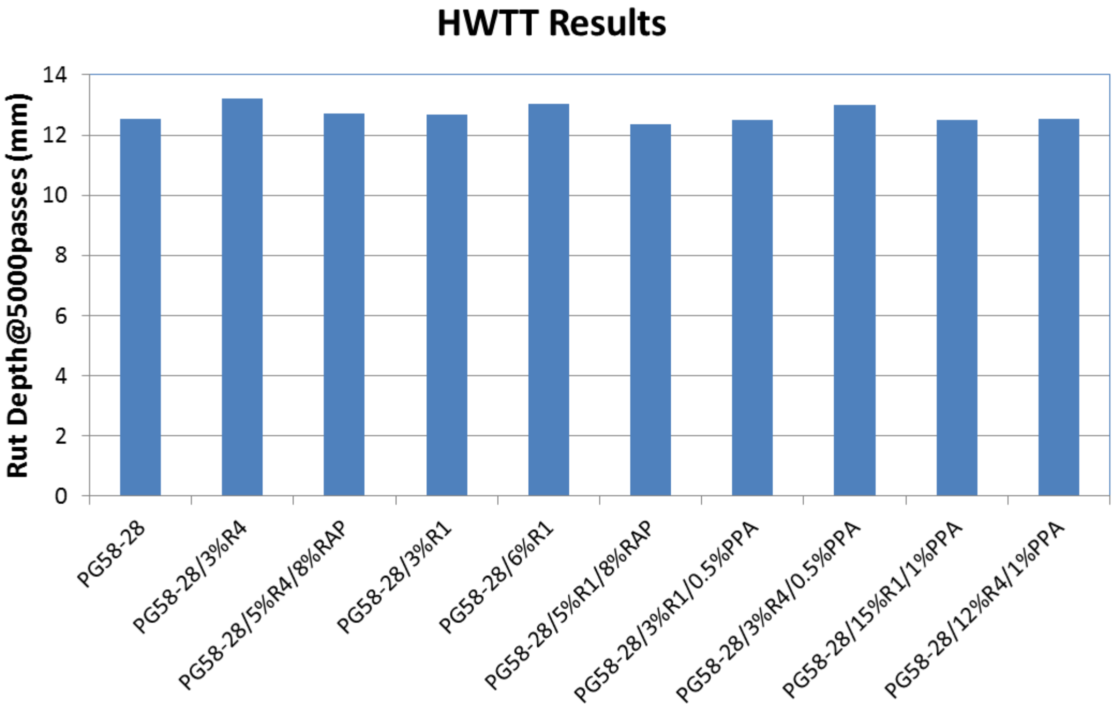


Figure 60. HWTT Results of Mixtures with PG58-28 Binders but Modified Differently.

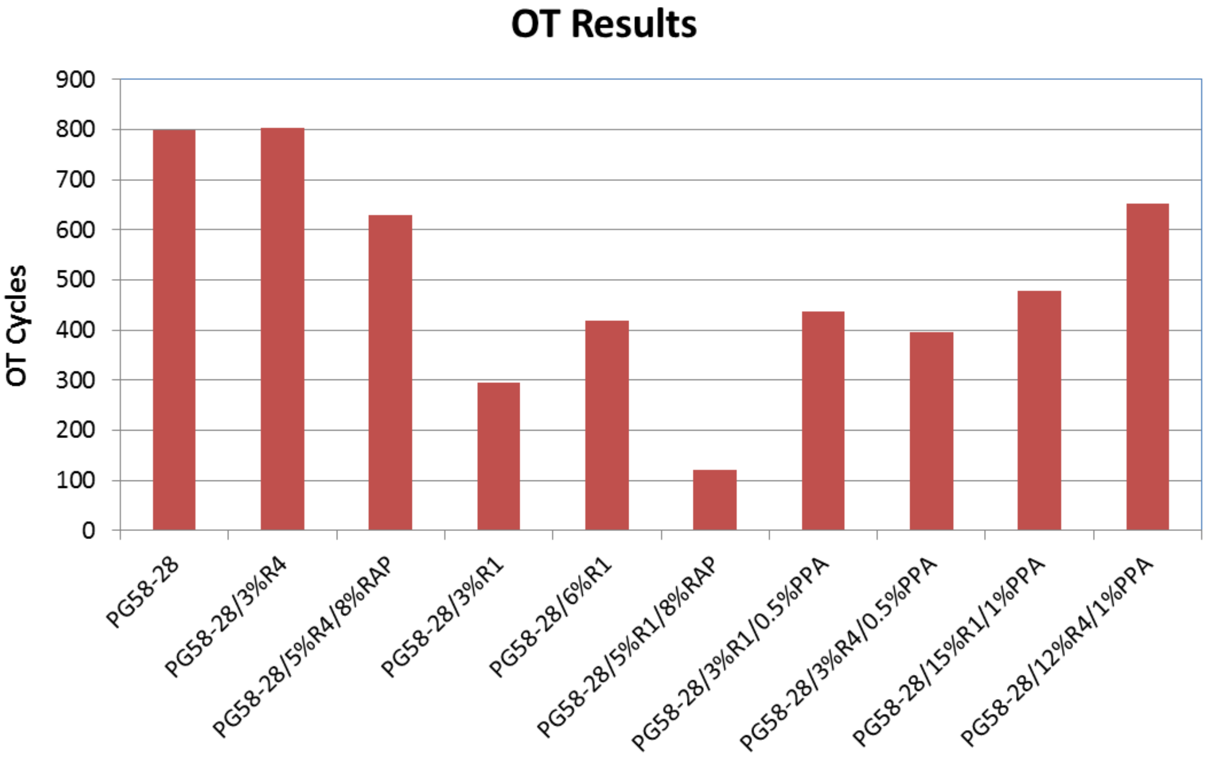


Figure 61. OT Results of Mixtures with PG58-28 Binders but Modified Differently.

SUMMARY

This chapter focused on the impact of REOB on asphalt mixture properties through HWTT, OT, IDEAL-CT, and Illinois SCB tests. The HWTT results for both virgin and RAP/RAS mixes illustrates that the addition of REOB to asphalt binder leads to poor rutting resistance of asphalt mixes, but the mixes still have acceptable rutting resistance as long as REOB content is controlled within 5 percent. For cracking resistance of asphalt mixes, it seems okay to add 5 percent REOB into asphalt binder without causing detrimental effect, but the mixes with 10 percent REOB somehow showed poor cracking resistance. Therefore, it is reasonable for TxDOT to maintain the current 5 percent upper limit for REOB in asphalt binders. To further evaluate the impact of REOB, the asphalt mixtures with 10 PG58-28 binders but modified differently were tested through both HWTT and OT. It was found that the mixtures with same PG grade binders could perform very differently in terms of cracking resistance. So it is critical to test the engineering properties of the final mixtures.

CHAPTER 7: IMPACT OF REOB ON SEAL COAT PERFORMANCE

Seal coats are the predominant tool Texas employs for pavement preservation, and every year TxDOT places more than 20,000 lane miles seal coats. There are many factors influencing seal coats performance. The most critical factor is the adhesion property of seal coat asphalt binder. To perform well, the seal coat binder must have a good adhesion property. Thus, this study investigated the impact of REOB on the adhesion property of seal coat binders.

LABORATORY EXPERIMENTAL DESIGN

A laboratory experiment was conducted to determine the effects of different quantities of REOB on adhesion properties of seal coat binders to seal coat aggregates. The tests used to evaluate these effects primarily consisted of the following:

- Cantabro Loss Test both dry and after moisture conditioning (a modification of Tex-245-F described below).
- Texas Boil Test (Tex-530-C).

The Cantabro Loss test is a test normally used to evaluate the raveling resistance of Permeable Friction Course mixtures. For the purposes of this project, Grade 5 seal coat aggregates were blended with seal coat binder at different quantities of REOB and compacted in a Texas Gyratory Compactor (Table 23). The Cantabro Loss test was performed on unconditioned samples and samples that were soaked in a 140°F water bath. After soaking for 24 hours, the specimens were air dried for one hour and cooled to room temperature prior to Cantabro Loss test. Each X in the testing matrix shown in Table 23 represents four specimens in most cases. Specimens were molded at 6.5 percent asphalt using an AC-10 modified with REOB as shown in Table 23.

Table 23. Cantabro Loss Testing Matrix.

% REOB	**Limestone**		**Gravel**		**70% Limestone/ 30% Gravel**	**50% Limestone/ 50% Gravel**
	Dry	24-hr soak	Dry	24-hr soak	24-hr soak	24-hr soak
0	X	X	X	X	X	X
5	X		X		X	X
10	X	X	X	X	X	X
15	X		X		X	
20	X	X	X	X		X
30	X	X	X	X		X

LABORATORY TEST RESULTS AND ANALYSES

Cantabro Loss Test Results and Discussion

Results of the Cantabro Loss testing are presented in Figure 62 through Figure 67. Figure 62 shows the test results performed in a dry condition using a limestone aggregate. From 0 to 20 percent REOB, less than 4 percent loss was observed. However, at 30 percent REOB, a significant increase to 9 percent loss was exhibited. While it appears that from 0 to 20 percent REOB, a slight decrease in loss was observed, this is attributed to the variability in the data. Each data point represents an average of four tests.

A similar trend is observed for the gravel aggregate specimens (Figure 63). From 0 to 20 percent REOB, less than 5 percent loss is observed. At 30 percent REOB, the Cantabro Loss significantly increased to 30 percent loss. In the dry condition, the limestone and gravel both experienced a significant increase in loss at 30 percent REOB but the gravel experienced much more than the limestone.

Figure 64 and Figure 65 show the results after the 24 hour soak. This type of sample conditioning shows the susceptibility of the materials to moisture damage. For the limestone specimens (Figure 64), a notable increase in Cantabro Loss begins at 20 percent REOB. For the Gravel specimens (Figure 65), the specimens essentially fell apart in the water both.

In terms of adhesion, limestone and gravel aggregates represent the two extremes in surface characteristics. To represent something in the middle of these two aggregate types, specimens were fabricated using a blend of 30/70 gravel/limestone and a 50/50 blend. While one would not typically combine aggregate sources for seal coats, the purpose was to simply fabricate a material to simulate aggregates that do not behave either as a limestone or gravel but something in between. These results are shown in Figure 66 and Figure 67, respectively. For the 30/70 blend, the detrimental effects of the REOB are observed beginning at 10 percent (Figure 66). For the 50/50 blend, the detrimental effects begin at 5 percent REOB (Figure 67).

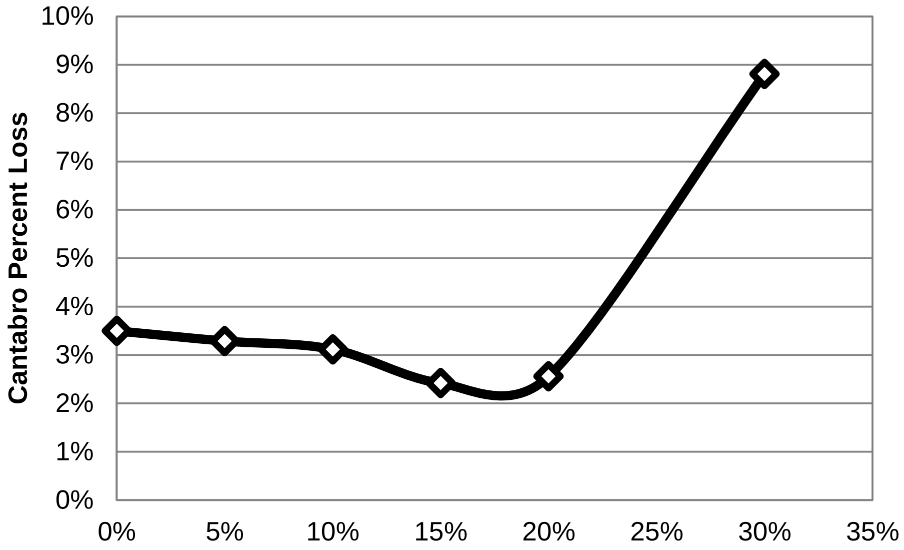


Figure 62. Cantabro Loss, Limestone Aggregate, No Conditioning (Dry).

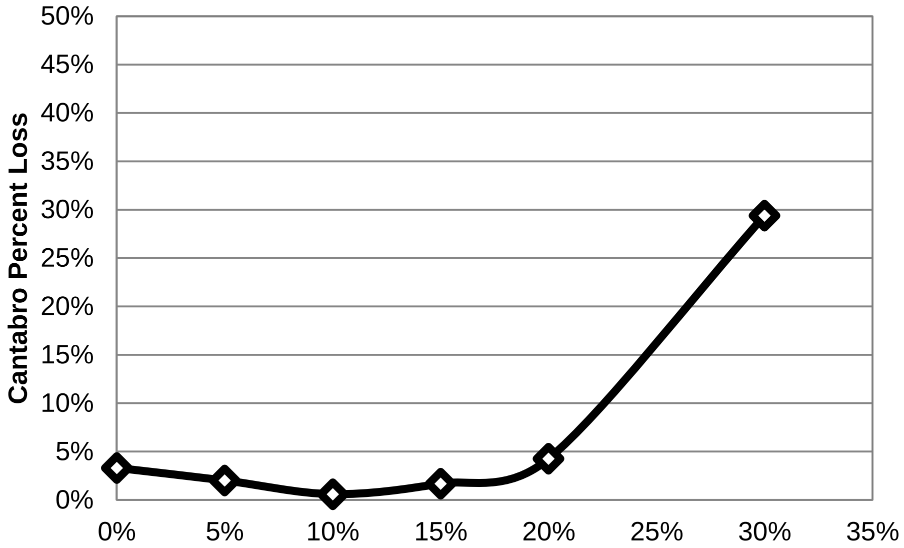


Figure 63. Cantabro Loss, Gravel Aggregate, No Conditioning (Dry).

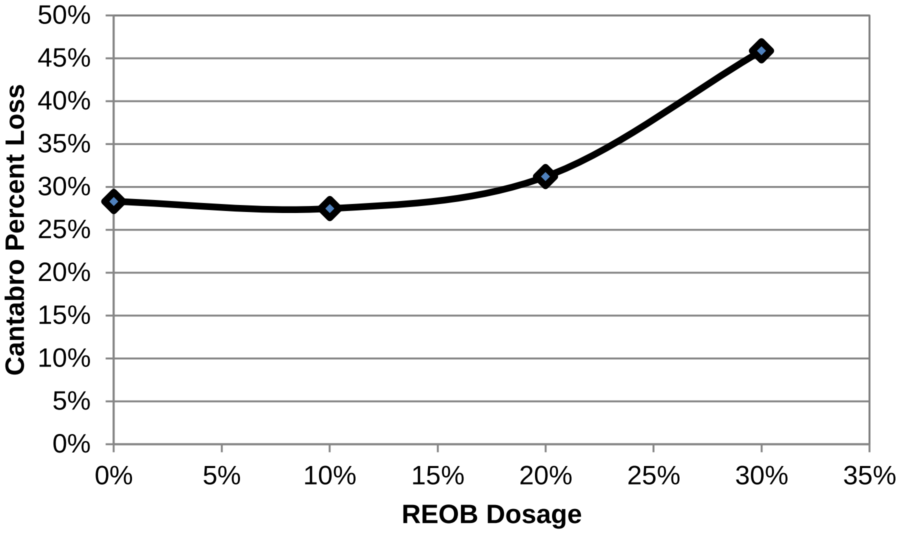


Figure 64. Cantabro Loss, Limestone Aggregate, 24-hr Soak.

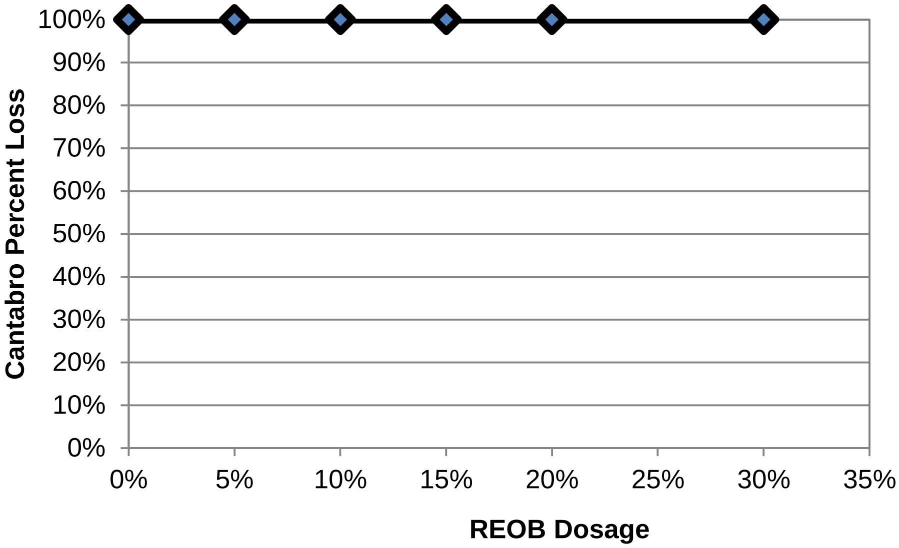


Figure 65. Cantabro Loss, Gravel Aggregate, 24-hr Soak.

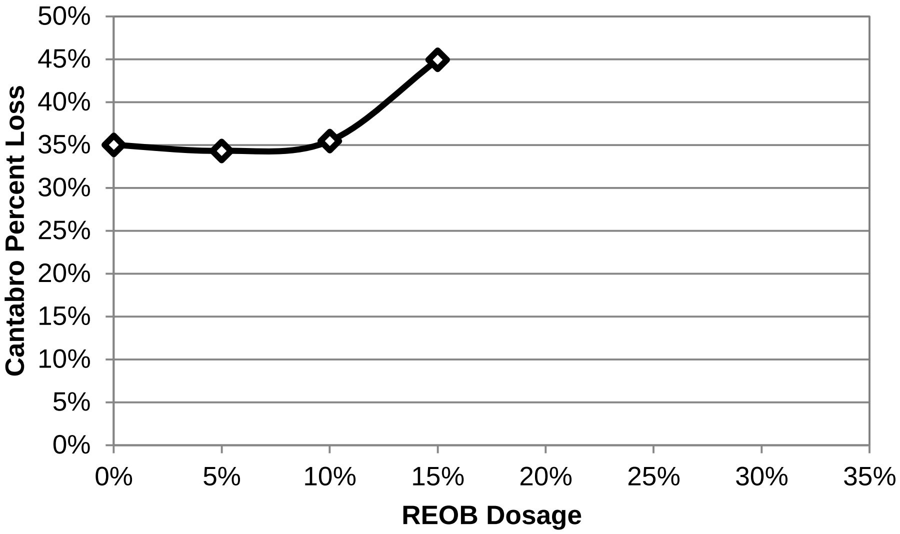


Figure 66. Cantabro Loss, 30 Percent Gravel/70 Percent Limestone Aggregate, 24-hr Soak.

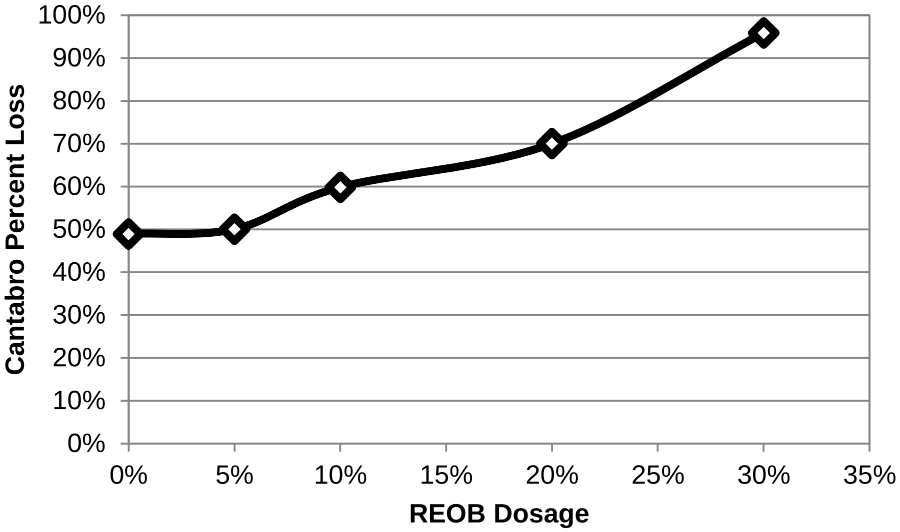


Figure 67. Cantabro Loss, 50 Percent Gravel/50 Percent Limestone Aggregate, 24-hr Soak.

The results of Figure 64, Figure 66, and Figure 67 are combined in Figure 68. In this figure, one can see where the detrimental effects of the REOB occur for each aggregate type:

- 100 percent limestone detrimental effects begin at 20 percent REOB.
- 70 limestone/30 gravel detrimental effects begin at 10 percent REOB.
- 50 limestone/50 gravel detrimental effects begin at 5 percent REOB.

Figure 69 shows the limits for the different aggregate types. This represents the maximum REOB quantity that may be tolerated based on the percent gravel used in our sample fabrication.

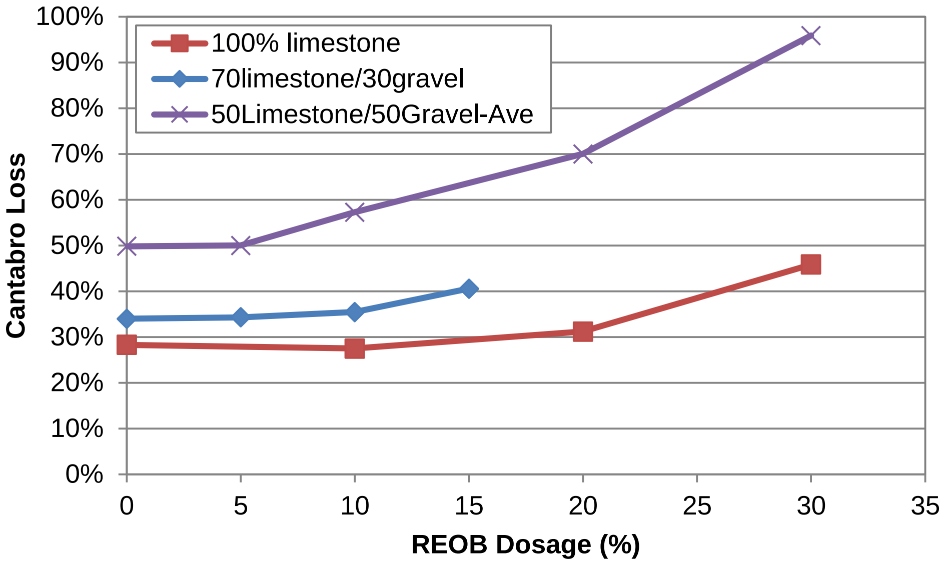


Figure 68. Cantabro Loss after 24-Hr Soak vs. %REOB for Different Aggregate Types.

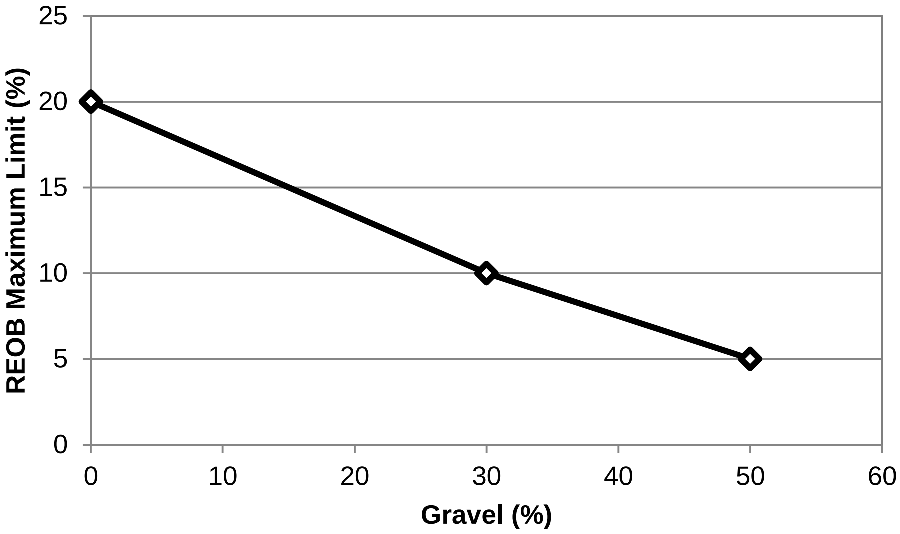


Figure 69. Maximum %REOB as Determined by Percent Gravel in the Aggregate Blend.

Boil Test Results and Discussion

The boil test (Tex-530-C) was conducted on the coated gravel and limestone blends with different quantities of REOB. This test is used to evaluate the susceptibility of hot mix paving mixtures to stripping of the asphalt from the aggregate by water. After the test is performed, the degree of stripping present by visual examination under slight magnification is estimated. Figure 70 through Figure 73 show photographs of some of the samples before and after testing. In addition, researchers actually weighed the specimens before and after testing to determine the quantity of asphalt that was lost due to stripping. Figure 74 shows these data.

Before Boil Test

After Boil Test

Figure 70. Boil Test Results for Gravel, 0 Percent REOB.

Before Boil Test

After Boil Test

Figure 71. Boil Test Results for Gravel, 10 Percent REOB.

Before Boil Test

After Boil Test

Figure 72. Boil Test Results for Limestone, 0 Percent REOB.

Before Boil Test

After Boil Test

Figure 73. Boil Test Results for Limestone, 10 Percent REOB.

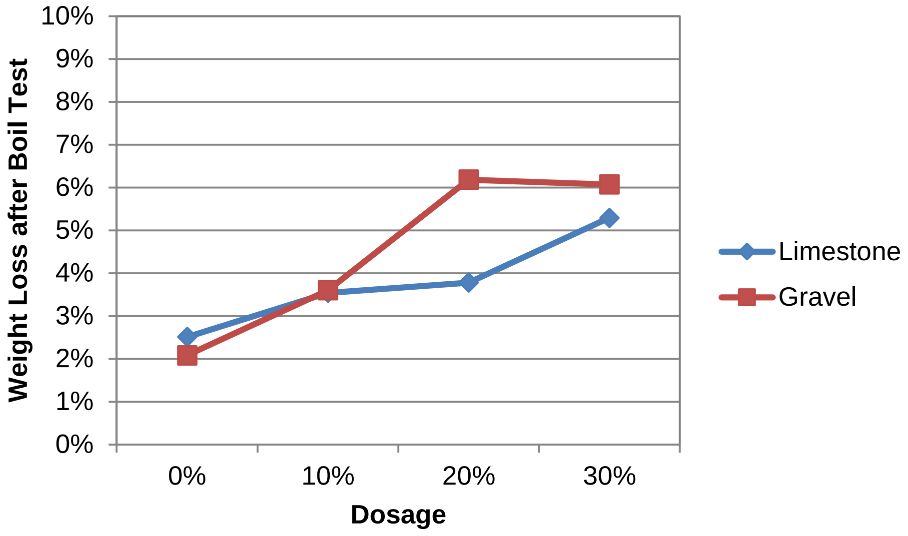


Figure 74. Boil Test Results for Different REOB Quantities.

SUMMARY AND RECOMMENDATION

Both the Cantabro Test and Boil Test results presented here show a negative effect on the adhesion characteristics of seal coat binders to aggregates due to the presence of REOB in the binder. The aggregate type appears to also be a factor in how detrimental the effects of the REOB will be. However, it is not practical to specify a REOB limit based on aggregate type being used; therefore, the results for the most vulnerable aggregates should be considered as the maximum limit. Based on the results presented here the following limit is recommended for seal coat asphalt binders:

$$\textbf{Maximum Allowable REOB Content for Seal Coat Asphalt}: \mathbf{5.0}\%$$

CHAPTER 8: SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Although asphalt binders used in these days still meet the requirements of the PG specification, many pavement engineers express the concerns on embrittlement and a lack of adhesion and tackiness of the asphalt binders. TxDOT became increasingly aware of these issues so that a new research on REOB was initiated to address it in 2015. The main objectives of this study were to (1) establish REOB detection method, (2) evaluate the impact of REOB on asphalt binder properties, asphalt mixture properties, and seal coat performance, and (3) recommend the maximum allowable amount of REOB in asphalt binders and seal coat binders. Researchers accomplished the three objectives through a series of laboratory tests. Based on the data presented in this report, both conclusions and recommendations are offered below.

CONCLUSIONS

Detection of REOB

1. **Presence/Absence:** The presence and intensities of Ca, Cu, K, Mo, Zn, and P elements measured from XRF can be used to determine whether or not REOB exists in asphalt binders and seal coat binders.
2. **Content Estimation**: Both the handheld and the benchtop XRF instruments can be used to estimate REOB/GTR in binders:
    a. **Asphalt Binders**: The estimation of REOB content in HMA binders can be conducted using the calibration curves of Ca/K ratio and Zn intensity following a three-step benchtop XRF-based method. The estimation of REOB content in HMA binders can be also conducted using the calibration curves of Ca, Mo, and Zn concentrations following a two-step handheld XRF-based method.
    b. **Seal Coat Binders**: The estimation of REOB/GTR content in HMA binders can be conducted using the calibration curves of Zn/Ca, Zn, and Mo following a four-step benchtop or handheld XRF-based method.

Effect of REOB

1. **Asphalt Binders:** REOB, AE, and BR all affect rheological, chemical, and structural properties of binders, and these effects depend on the type, the source and the dosage of selected modifier, the source and grade of base binders, and presence of RAP- or RAS-extracted binders. As such, PG specification alone does not guarantee well performing binders. The embrittlement parameter (ΔT_c) and the rheological index (R) values clearly differentiate REOB from other type of modifiers.
2. **Asphalt Mixtures**: The addition of REOB to asphalt binder leads to poor rutting and cracking resistance of asphalt mixes, but the mixes still have acceptable rutting and cracking resistance as long as REOB content is controlled within 5 percent. The mixtures with same PG grade binders could perform very differently in terms of cracking resistance. So it is critical to test the engineering properties of the final mixtures.
3. **Seal Coats**: REOB degrades adhesive property of seal coat binder. The detrimental effect depends on the type of aggregate type as well. Therefore, most vulnerable aggregates should be considered while specifying maximum allowable REOB content in seal coat binders.

RECOMMENDATIONS

1. **REOB detection:** TxDOT should consider to use either the benchtop or handheld XRF instrument to detect REOB in asphalt binders or seal coat binders using the methods presented in this report. In terms of accuracy, both types provide almost similar estimations. TxDOT can make the choice between handheld or benchtop XRF based on intended level portability, availability, and cost of the instruments. For field applications, handheld XRF is recommended due to its practicality. It is also recommended that TxDOT make these methods more inclusive by adding standards when a new binder or REOB source in Texas binders in future.
2. **Binder embrittlement parameter** (ΔT_c): TxDOT should consider to modify asphalt binder specification to incorporate binder embrittlement parameter, ΔT_c, which is the most effective rheological parameter to determine the detrimental effect of REOB on asphalt binders.
3. **REOB upper limit for asphalt binders:** TxDOT should maintain the current 5 percent upper limit for REOB in asphalt binders.
4. **REOB upper limit for seal coat binders:** TxDOT should limit the REOB in seal asphalt binders at 5 percent or even less for more vulnerable aggregates.

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