RE-REFINED ENGINE OIL BOTTOMS (REOB) & POLYPHOSPHORIC ACID (PPA) IN HOT MIX

89th Annual Transportation Short Course
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**What is REOB?**

- **Re-refined Engine Oil Bottoms (REOB)**
  - Obtained from refining recovered engine oils
    - Non-distillable fraction
  - REOB used in paving since the 1980s
    - Approximately 160,000 tons are produced each year
  - Recommended dosage is 6-8%
    - CST testing indicates some asphalts contain 15% or more
  - Modifies the low temperature property of the binder
    - PG64-22 ➔ PG58-28 or PG64-28
    - Softer grades are needed with recycled materials (RAP/RAS)

*Source: The Association of Modified Asphalt Producers (1)*
What is PPA?

- **Polyphosphoric Acid (PPA)**
  - Produced by the addition of sulfuric acid to phosphate rock
  - First patent for binder modification filed in 1973
  - Approximately 10,000,000 tons are produced each year
    - Most (80%) is used in the production of fertilizers
  - Modifies the high temperature property of the binder
    - PG64-22 ➔ PG70-22 or PG76-22

Sources: Sunkar Resources (2) and (3,4)
Potential Problems Associated with Using REOB and PPA

- **REOB**
  - Stability Issues
    - Rutting
  - Raveling
  - Premature Cracking
    - Thermal
    - Fatigue
  - Physical hardening
    - Increased stiffness when stored at a constant low temperature

- **PPA**
  - Negative interactions with lime and liquid anti-stripping agents
    - Stripping
    - Rutting

Highway 41 in Ontario Containing REOB (5)

Highway 655 in Ontario Containing REOB (6)

Source: (3), (5) and (6)
Some Evidence in Texas

- **Laboratory and Field Problems**
  - Hamburg failures
    - Several iterations were performed without success
    - Solution was to change asphalt source
  - Forensics
    - Premature failures including raveling, color change, cracking, aging
    - Many of these mixtures did not contain recycled material
  - Some issues pointed to binder quality
    - Binder rheology did not pick up the problems
    - Needed a different method of analyzing binders

Photo taken July 28, 2014

Photo taken Aug. 26, 2014
Nationwide Perspective on REOB and PPA

- **REOB**
  - Since 2010 some municipalities in the Province of Ontario in Canada have banned REOB
  - In 2014 state DOTs in New England banned the use of REOB
    - More states are becoming aware
  - Recent survey by AASHTO reported 71% of states had no specification for using REOB

- **PPA**
  - Pennsylvania DOT (2002, 2008) and Ontario Ministry of Transportation 2007 Surveys
    - 12 states no restrictions
    - 15 states have banned the use of PPA
    - 14 have restrictions
    - 7 remain neutral

Source: (1,3)
Special Provision 300-009

- **REOB**
  - Beginning in August 2015 letting, TxDOT specification limit is 5.0% by weight of the asphalt binder for Performance-Graded Binders

- **PPA**
  - Beginning in August 2015 letting, TxDOT specification limit is 0.5% by weight of the asphalt binder for Performance-Graded Binders
TxDOT’s WDXRF Spectrometer

- Needed a method to detect and quantify REOB and PPA
- Wavelength Dispersive X-Ray Fluorescence (WDXRF) Spectroscopy
  - Rigaku ZSX Primus II 4kW spectrometer
- Elemental Analysis
  - Determine the elemental contributions of REOB and PPA by analyzing asphalt samples with and without REOB and PPA
What’s in Lubricating Oil and PPA?

- What are some elements are in lubricating oil?
  - Wear metals
    - Tin, Lead, Copper, Aluminum, Iron, Chromium, Silver, Nickel, Vanadium, Molybdenum, and Manganese
  - Oil additives
    - Lead, Copper, Silicon, Zinc, Molybdenum, Magnesium, Barium, Sodium, Calcium, Phosphorus, and Boron
  - Antifreeze additives
    - Silicon, Chromium, Sodium, Phosphorous, Boron, and Potassium
  - Contaminants
    - Aluminum, Silicon, Magnesium, Nickel, Sodium, Calcium, Vanadium, Phosphorous, Boron, and Potassium

- What are some elements in PPA?
  - Chemical formula = $H_3PO_4$
    - Phosphorous

Source: Metro Tech Systems Ltd. (7)
## Elemental Differences in REOB and PPA Samples

<table>
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<tr>
<th>Virgin Asphalt</th>
<th>Asphalt With REOB</th>
<th>Asphalt With PPA</th>
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<tbody>
<tr>
<td>- Iron (Fe)</td>
<td>- Iron (Fe)</td>
<td>- Iron (Fe)</td>
</tr>
<tr>
<td>- Nickel (Ni)</td>
<td>- Nickel (Ni)</td>
<td>- Nickel (Ni)</td>
</tr>
<tr>
<td>- Sulfur (S)</td>
<td>- Sulfur (S)</td>
<td>- Sulfur (S)</td>
</tr>
<tr>
<td>- Vanadium (V)</td>
<td>- Vanadium (V)</td>
<td>- Vanadium (V)</td>
</tr>
<tr>
<td></td>
<td>- <strong>Phosphorus (P)</strong></td>
<td>- <strong>Phosphorus (P)</strong></td>
</tr>
<tr>
<td></td>
<td>- Molybdenum (Mo)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Zinc (Zn)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Copper (Cu)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Potassium (K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Calcium (Ca)</td>
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**Question:** Do the intensities of these elements correlate with concentration?
Example of REOB Calibration Standard

\[ y = 2.7123x + 5.5015 \]
\[ R^2 = 0.9966 \text{ (Mo)} \]

\[ y = 0.343x + 0.838 \]
\[ R^2 = 0.9979 \text{ (Cu)} \]

\[ y = 3.3953x + 2.4175 \]
\[ R^2 = 1.0000 \text{ (Ca)} \]

Intensity (kcps)

0 5 10 15 20 25

REOB (%)
Example of PPA Calibration Standard

\[ y = 114.07x - 0.849 \]

\[ R^2 = 0.9979 \text{ (P)} \]
Summary

- **Detection**
  - REOB and PPA are easily detected using XRF

- **Quantification**
  - More challenging
    - Crude source has an effect on REOB quantification
      - Less effect for PPA
    - REOB sources are not the same
      - Contain different amounts of elements
    - REOB consistency is unknown
      - Less error observed for PPA

Source: Arnold and Gibson (8)
Future Direction

- Further refining the process to increase accuracy
  - Determine if there are key elements present in all asphalt samples that may normalize the data to reduce the error
    - Sulfur, Vanadium, Iron, and Nickel were observed in all asphalt samples
    - Sulfur and Vanadium gave the best correlation to reduce the error
  - Increase the number of standards
    - Vary the amount of sulfur and vanadium
Sulfur Vs. Vanadium

- Sulfur (kcps)
- Vanadium (kcps)

Legend:
- QM/Project
- A1R1 Cal. Std.
- A2R1 Cal. Std.
- A3R1 Cal. Std.
- A7R1 Cal. Std.
Future Direction

- Further refining the process to increase accuracy
  - Monitor REOB composition over time
    - Determine how consistent REOB is from same source
  - Determine if REOB source can be determined
    - Manganese (Mn) may be key
    - Absence or presence of other elements
    - Ratio of element intensities (e.g. Zinc/Copper)
  - Beginning to look at AC binders for seal coats
    - Hot applied seal coat binders
  - Projects (e.g. seal coats, HMA, WMA, etc.) having trouble?
    - Send in a sample for testing
Future Direction

- Look at other binder test methods
  - Center for Transportation Research (CTR)
  - Look at non-standard binder tests
    - Current PG binder tests are not addressing the problems
  - Potential replacement for SP300-009
    - Effect of PPA and REOB depends on base binder
    - Performance based test decides the amount of REOB and PPA allowed instead of prescribed amount

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<th>Test Method</th>
<th>Remarks</th>
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<tr>
<td>MSCR (at multiple temperatures)</td>
<td>Previous tests have shown that certain binders that contain PPA also have an abnormally high true grade based on the non-recoverable compliance criterion of 4.0 1/MPa.</td>
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<td>BBR (at low temperatures for stiffness and m-value)</td>
<td>Anomalies in the low temperature properties can serve as indicators of modifications that may result in a non-durable binder.</td>
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<tr>
<td>Spot Test (T209)</td>
<td>A separation test and compatibility indicator for binder components.</td>
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<tr>
<td>Poker Chip Test</td>
<td>A simple binder fracture test that measures a materials resistance to fracture.</td>
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<tr>
<td>Mortar Test</td>
<td>Measures the fatigue cracking resistance of the asphalt binders in an asphalt mortar. The test was implemented as a diagnostic tool by TxDOT in 2008.</td>
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<tr>
<td>SARA / Corbett fraction (ASTM D4124)</td>
<td>Indicates the relative proportions of different polar fractions in the asphalt binder. Binders with relatively high fractions of extreme polar fractions are very likely to be unstable in field performance.</td>
</tr>
<tr>
<td>Fluorescence Microscopy</td>
<td>Used to assess compatibility and distribution of polymers and other fractions within the asphalt binder.</td>
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### Future Direction

- **TxDOT Project 0-6881 with Texas Transportation Institute (TTI)**

| Task 1 | Assemble Background Information |
| Task 2 | Webinars with National Experts on REOB in Asphalt and Seal Coat Binders |
| Task 3 | Purchase Handheld Units |
| Task 4 | Methodology for Determining REOB and PPA Content in Asphalt Binders with Benchtop and handheld XRF |
| Task 5 | Define Maximum Allowable REOB and PPA in HMA Based on Engineering Properties |
| Task 6 | Influence of REOB on Oxidative Aging |
| Task 7 | Determine REOB Content in Hot Applied Seal Coat Binders |
| Task 8 | Define Maximum Allowable REOB Use in Hot Applied Seal Coat Binders |
| Task 9 | Field Evaluation in Districts |
| Task 10 | Implementation Recommendations for Receiving Agency |
| Task 11 | Project Management |
Acknowledgements

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QUESTIONS?
References