Sulphur’s Place in CE
Foundation Performance Association, Houston

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Technology - Delivery - Partnership
Presentation Topics

• Why sulphur?
• New approaches to using sulphur
  – Thiocrete®
  – Thiopave®
Sulphur (Sulfur)

- Non-metallic element, S, atomic number 16
- Though naturally occurring, most elemental sulphur produced today is from natural gas and petroleum processing
- USA, Canada, former Soviet Union, West Asia are primary producers
  - Canada, Russia, Saudi Arabia chief exporters
- USA, China are largest consumers
- Worldwide sulphur production expected to increase dramatically in the next 10 years
Sulphur uses (from TSI)

The major derivative of sulphur is sulphuric acid (H₂SO₄), the highest production volume chemical, used as an industrial raw material. The largest single use of sulphuric acid is for the manufacture of phosphoric acid, a precursor to phosphate fertilizers and non-fertilizer phosphates. Sulphur and its derivatives are also used in metallurgical ore leaching, caprolactam, pigments, hydrofluoric acid, pulp and paper chemicals, sulphur fertilizers, petroleum refining, batteries, detergents, fungicides, carbon disulphide, pharmaceuticals, personal care products, cosmetics, leather tanning, rubber vulcanization, plasticizers, dyestuffs, explosives, aramid fibers, construction materials, sugar manufacture, dehydrating agent in organic chemical and petrochemical processes, water treatment, and steel pickling.
Sulphur as a construction material

- Sulphur concrete (Shell Thiocrete®)
  - Patented technology for using sulphur as a replacement binder for Portland cement for many pre-cast concrete applications

- Sulphur-enhanced asphalt (Shell Thiopave®)
  - Improved sulphur-extended asphalt technology
Shell Thiocrete-Benefits

- High strength
- Rapid curing
- Resistance to water and acid
- Tolerant of wide range of aggregate properties
  - Can use lesser-quality aggregates than possible with conventional PCC
- Enabling a wide range of colors, textures and finishes
- Easy to recycle
- Requires no water
- Significantly lower carbon footprint than Portland cement
Shell Thiocrete-Potential Applications

- Sea walls, riprap, jetty blocks
- Pavers, pre-cast curbs
- Road barriers and bollards
- Retaining walls
- Garden products
Shell Thiocrete-How it’s used

• Product to be supplied in liquid or pellet form
• Mixed with aggregate @ 275F (135C)
  – HMA plant
• Poured into molds
• When cooled to ambient temperature, it’s ready for use
  – No chemical reaction, curing is when the molten sulphur “freezes” into a solid
• To recycle, simply heat to melt sulphur then recast
Shell Thiocrete—What’s next?

- First commercial agreement established w/Dutch pre-cast company that makes paving stones for western European market
- Will work with suppliers/fabricators of pre-cast concrete to identify opportunities
Shell Thiopave

- Solid pellets, ~ 97% sulphur
  - Includes plasticizers, compaction agent and fume suppressants
- Can be stored on the ground or in silos
  - No concern with moisture during storage
- Blended with the mixture, not directly with asphalt binder
- Melts in hot-mix plant, disperses into mixture
- Keep temperature below 285F
Effects of Thiopave Modification

• Partial replacement of asphalt binder
  – 20-25% reduction in bitumen demand
  – Increased stiffness at high service temperatures, reduced temperature susceptibility
  – Improved resistance to rutting/permanent deformation

• No significant effect on cracking
  – Ability to increase total binder content and use softer binders may prove to improve resistance to thermal and fatigue cracking
Thiopave Binder Content Formula

Determination of mass percentage of total binder (Thiopave + Bitumen) to yield the same binder volume as in an existing asphalt mixture design:

\[ P_{bt}, \text{ Total Combined Binder, \% mass} = \frac{P_{b} \times 100R}{\left[100R - F_{Th}(R - G_{b})\right]} \]

Where:

- \( G_{Th} \) = Specific gravity of Thiopave
- \( F_{Th} \) = Percentage of Thiopave in total binder (typically, 30-40%)
- \( R \) = Thiopave to bitumen substitution ratio
  - \( = G_{Th}/G_{b} \) for equivalent binder volume*
- \( P_{Th} \) = Percentage of Thiopave by mass of mixture = \( P_{bt} \times F_{Th} \)
- \( P_{bm} \) = modified \% bitumen by mass of mixture = \( P_{bt} - P_{Th} \)

* A lower ratio as low as 1.7 may be used for “rich” mixes.
Example Calculation

Assume: $P_b = 5.3\%$

$F_{Th} = 40\%$ (ie. $40\%$ Thiopave/$60\%$ Bitumen blend by mass)

$G_{Th} = 2.00$

$G_b = 1.03$ $\Rightarrow R = \frac{2.00}{1.03} = 1.94$

$P_{bt} \% = 5.3\left\{\frac{100 \times (1.94)}{100(1.94) - (40)(1.94-1.03)}\right\} = 5.3 \times 1.23^*$

$= 6.6\%$

$\therefore P_{Th} = 2.6\%, P_{bm} = 4.0\%$
Effect on Marshall Stability
PG 58-28, Fine-Graded Aggregate

Marshall Stability increases with Thiopave content
Marshall Stability Comparison

Qatar Test Road Results

>10% higher initially, over 80% higher after 14 days

>1800 lbs

Conventional Mix

Thiopave

1 Day

14 Days
Comparison of HWT (50C) Results for Port of Oakland, Thiopave and Heavy-Duty HMA

Example HWT Specification Criteria, PG 76-22:

1. Colorado DOT: rut depth less than 10 mm
2. Texas DOT: rut depth less than 12.5 mm
Asphalt Pavement Analyzer (APA) Specimens after 8000 passes

<table>
<thead>
<tr>
<th>“Sandy” aggregate gradation</th>
<th>Crushed aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional HMA</td>
<td>Thiopave-modified HMA</td>
</tr>
</tbody>
</table>

Asphalt Binder: PG 58-28
Temperature Sensitivity

- Thiopave-modified mixtures are *much stiffer* at high temperatures than conventional HMA
- Minimal difference in stiffness at low temperatures
- Conclusion: The stiffness of Thiopave mixtures is less sensitive to temperature changes than conventional HMA

Control
Thiopave-modified

Resilient Modulus, MPa

Frequency = 1 Hz

Temperature, C
Sensitivity to Loading Time

- Greater stiffness at lower speed
  - More rut-resistant
  - Structural improvement
    - Less flexural strain
    - Less vertical compressive strain @ top of subgrade
- Thiopave is less affected by changes in the loading rate than conventional

\[ T = 30^\circ C \]
Master Curves (NCAT)
E* vs Frequency, after 1 day

Dynamic Modulus (E*) (MPa)

- 0% SEAM 4% Design Va
- 30% SEAM 3.5% Design Va
- 40% SEAM 3.5% Design Va
E* vs Frequency, after 14 days

![Dynamic Modulus (E*) vs Frequency graph]

- 0% SEAM 4% Design Va
- 30% SEAM 3.5% Design Va
- 40% SEAM 3.5% Design Va
Fatigue Testing, Port of Oakland

![Graph showing tensile stress vs. number of cycles to failure for Thiopave and "Heavy-duty" HMA.](image-url)
Effect of Thiopave on Thermal Stress Restrainted Specimen Tests (TSRST) Results

TSRST Comparison

Note: Thiopave Mixtures: 40% Thiopave/60% Bitumen
Production-Feed System

- Developing a pneumatic feed system for Thiopave pastilles
- Best to feed them at/near baghouse fines return
Production

Requires strict temperature control
~ 135°C (275°F) is ideal
HS&E - Sulphur

- Non-toxic
- Does not leach
- Does not react at ambient temperatures
HS&E – Emissions at HMA Plant

ASPHALT HOT-MIX PLANT:

$H_2S \& SO_2 = 0$ AT MIXER AND TRUCK LOADING AREA

Six Hour Average, Oct. 2002
HS&E – Emissions at the Paver

Six Hour Average, Oct. 2002

<table>
<thead>
<tr>
<th></th>
<th>H₂S</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASPHALT PAVER:</td>
<td>0.9 PPm</td>
<td>0 PPm</td>
</tr>
<tr>
<td>ABOVE SCREED (1):</td>
<td>0.9 PPm</td>
<td>0 PPm</td>
</tr>
<tr>
<td>OPERATOR PANEL (2):</td>
<td>0.1 PPm</td>
<td>0.3 PPm</td>
</tr>
<tr>
<td>AVERAGE LIMIT (2002 TLV):</td>
<td>10 PPm</td>
<td>2 PPm</td>
</tr>
</tbody>
</table>
## HS&E - Emissions

### Reduced Hydrocarbon Content and Temperature Results in Greatly Reduced VOCs

<table>
<thead>
<tr>
<th>Date and conditions</th>
<th>Total VOC ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug 15: Downwind, 5m; Control HMA produced @ 152C</td>
<td>214</td>
</tr>
<tr>
<td>Aug 15: Upwind, 5-m; Control HMA @ 152C</td>
<td>257</td>
</tr>
<tr>
<td>Aug 16: Breathing zone; Thiopave mix produced @ 140C</td>
<td>98</td>
</tr>
<tr>
<td>Aug 16; Downwind, 5m, Thiopave mix produced @ 140C</td>
<td>99</td>
</tr>
</tbody>
</table>
Greenhouse Gases

• Reduced hydrocarbon concentration and temperature reduces CO$_2$ footprint
• Blue Source Study (Alberta)
  – Developing methodology to properly document carbon footprint of paving materials
  – Sea-to-Sky (British Columbia) field validation
Potential Applications & Limitations

**Applications:**
- Stiff, rut resistant layers
  - High modulus asphalt base course
  - Perpetual Pavement structural layers
- “Black” Bases
- Ports, intermodal terminals, container loading facilities
  - Any paving application where RCC would be considered
- Intersections

**Limitations:**
- MUST be able to control temperatures during production!
  - Don’t expose sulphur to temperatures exceeding 285F!
- Do NOT use with:
  - Polymer-modified bitumens
  - Mixtures using hydrated lime or Portland cement fillers
- Don’t use in thin-surfaced flexible pavements
Ongoing Research

• Projects in British Col., California
• Full-scale test tracks
  – NCAT (2 sections)
  – Louisiana ALF (2 sections)
• Laboratory
  – NCAT, LTRC
  – Commercial laboratories
• HS&E
  – Blue Source (Canada)

Structural Performance

Material Properties, Local Materials Q’s & A’s

Stay tuned, much more to come!
Conclusions

• Thiopave provides a safe, practical and economic way to enhance asphalt mixture qualities with sulphur
• Thiopave is a viable alternative for producing heavy-duty mixtures
• Shell is firmly committed to developing civil engineering applications for elemental sulphur