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 (H_2SO_4), 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*, <u>not</u> 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}, Total Combined Binder, % mass =

$$\frac{P_b \times 100R}{\left[100R - F_{Th}\left(R - G_b\right)\right]}$$

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} * 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*)

$G_{Th} = 2.00$

$G_b = 1.03 \Rightarrow R = 2.00/1.03 = 1.94$

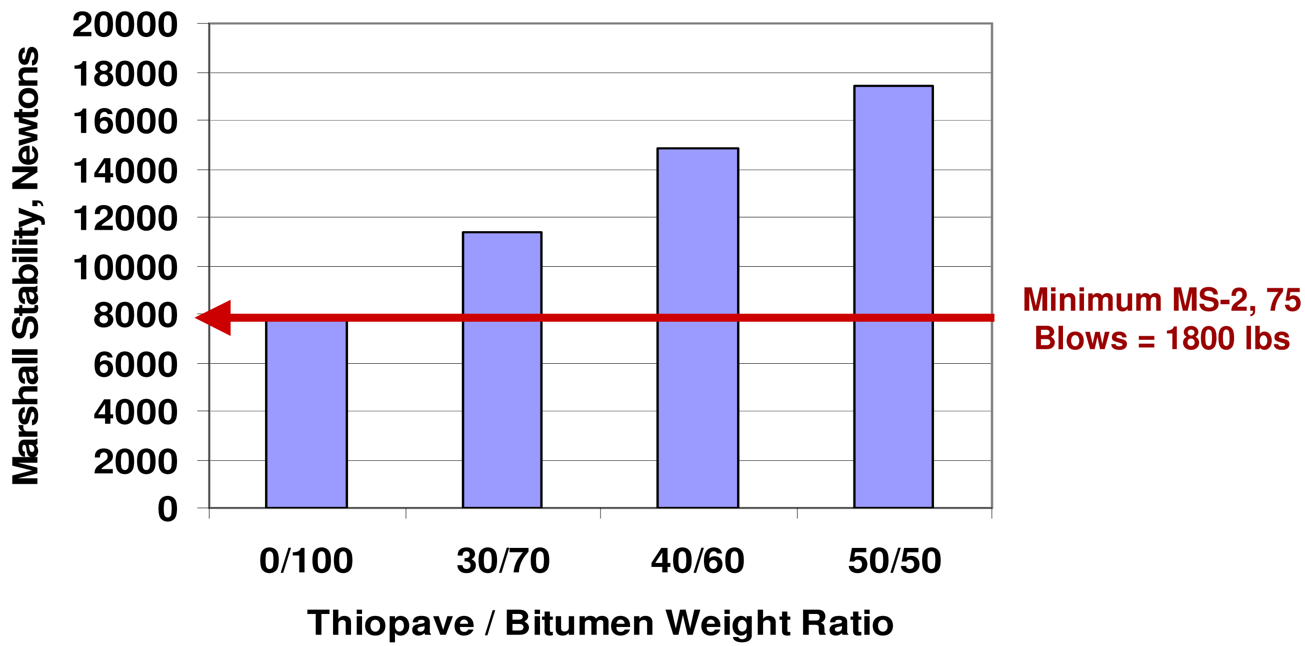
$$P_{bt}\,\% = 5.3\left\{\frac{100\,(1.94)}{100(1.94) - (40)(1.94-1.03)}\right\} = 5.3\,\{1.23\}^{*}$$

$$= \underline{6.6\%}$$

$$\therefore\ \mathbf{P_{Th} = 2.6\%,\ P_{bm} = 4.0\%}$$

Effect on Marshall Stability

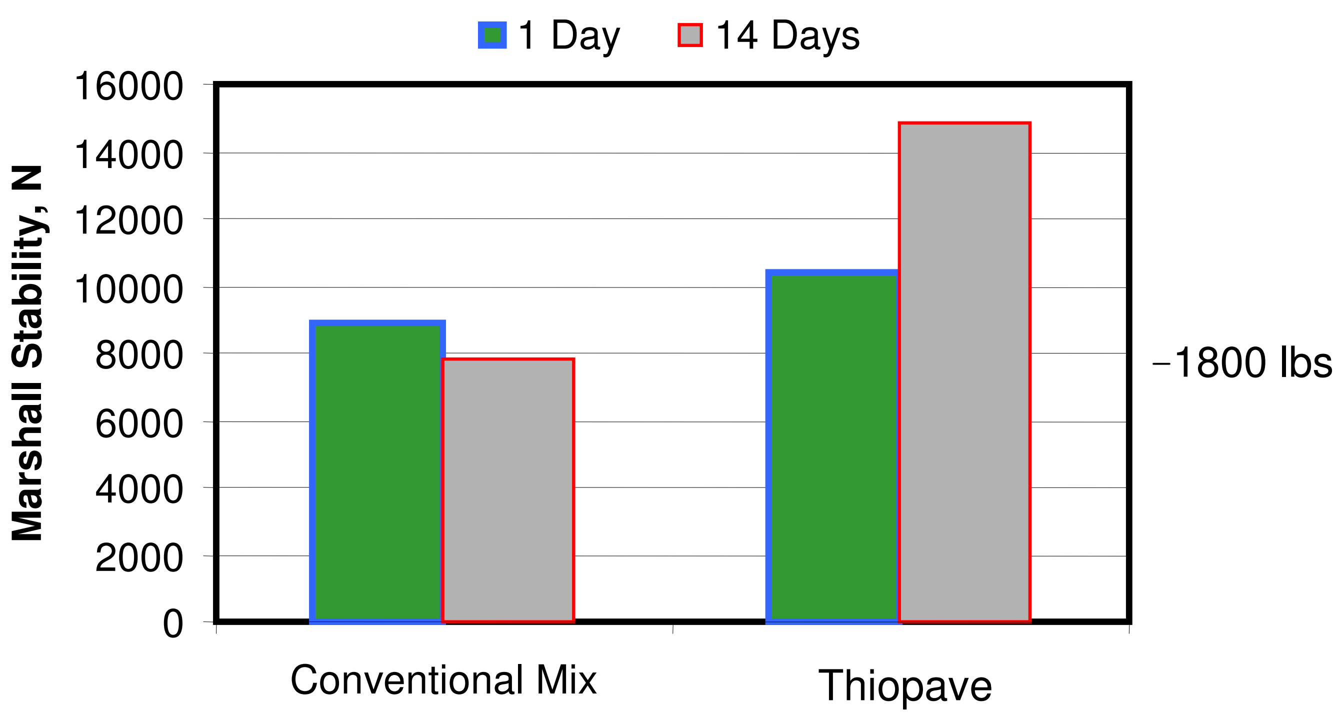
PG 58-28, Fine-Graded Aggregate



Marshall Stability increases with Thiopave content

Marshall Stability Comparison

Qatar Test Road Results



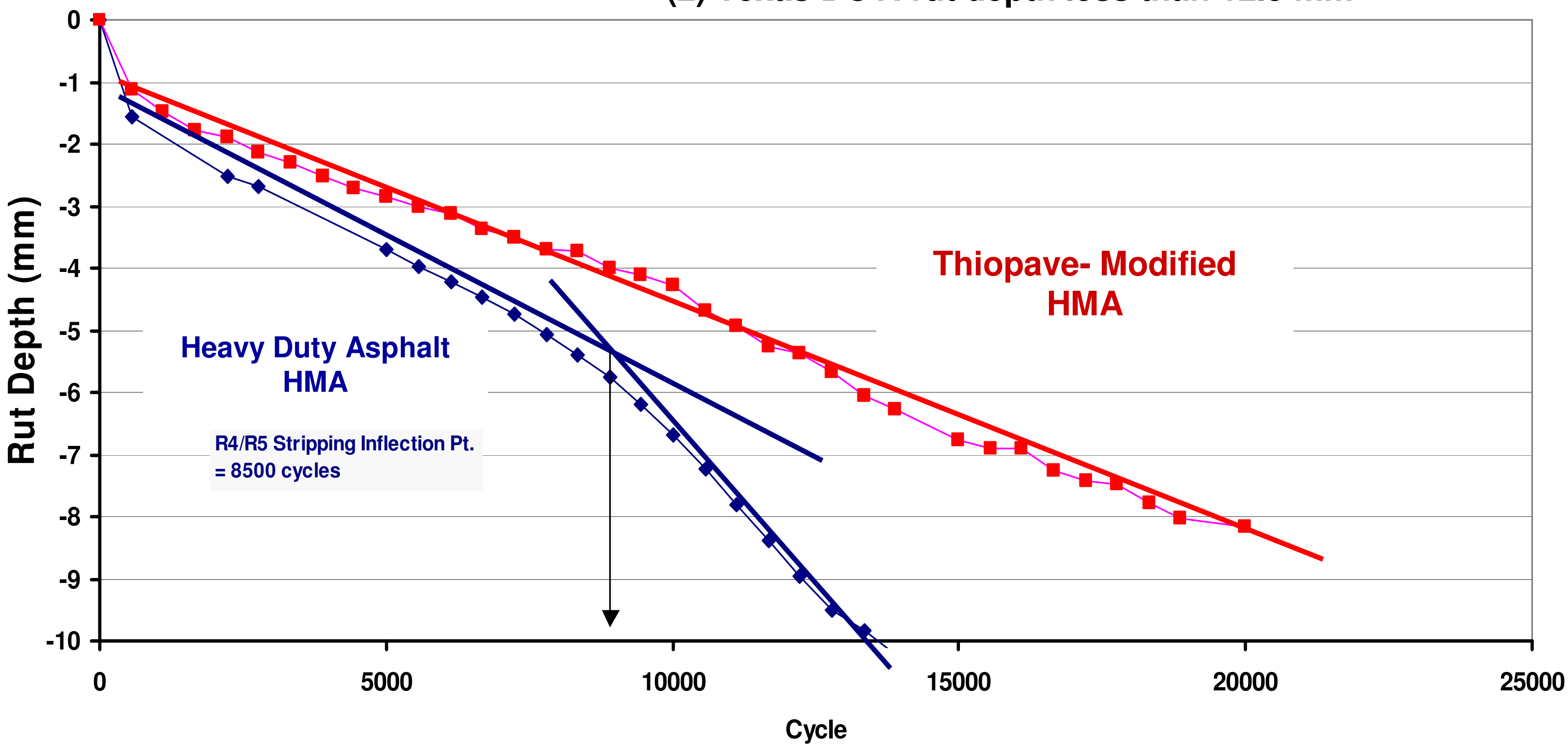
>10% higher initially, over 80% higher after 14 days

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

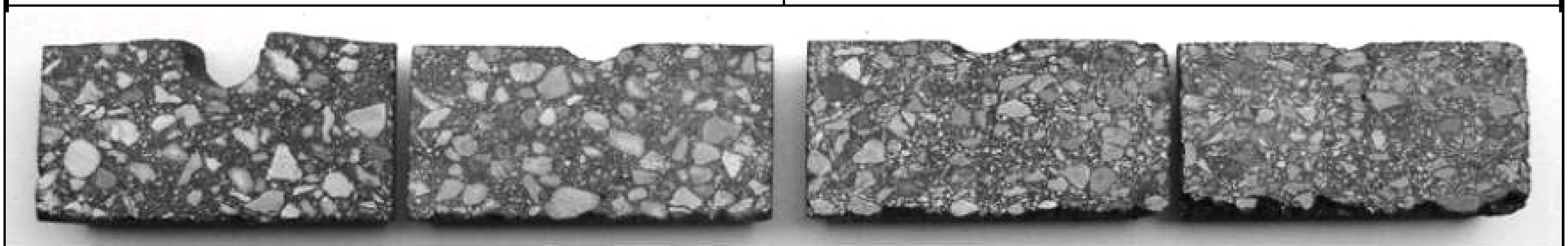
Example HWT Specification Criteria, PG 76-22:

(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>
<tr><th colspan="2">“Sandy” aggregate gradation</th><th colspan="2">Crushed aggregate</th></tr>
<tr><td colspan="4"></td></tr>
<tr><td>Conventional HMA</td><td>Thiopave-modified HMA</td><td>Conventional HMA</td><td>Thiopave-modified HMA</td></tr>
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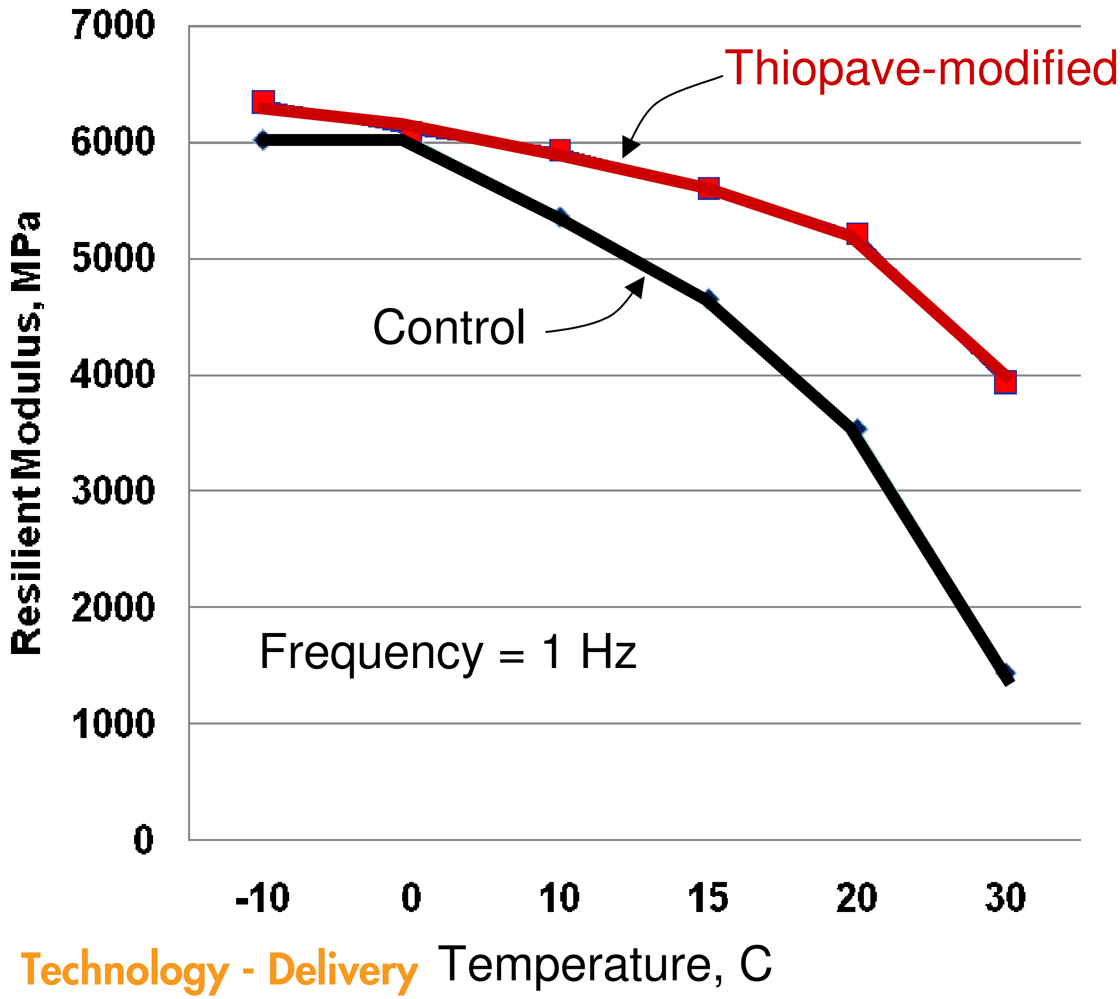
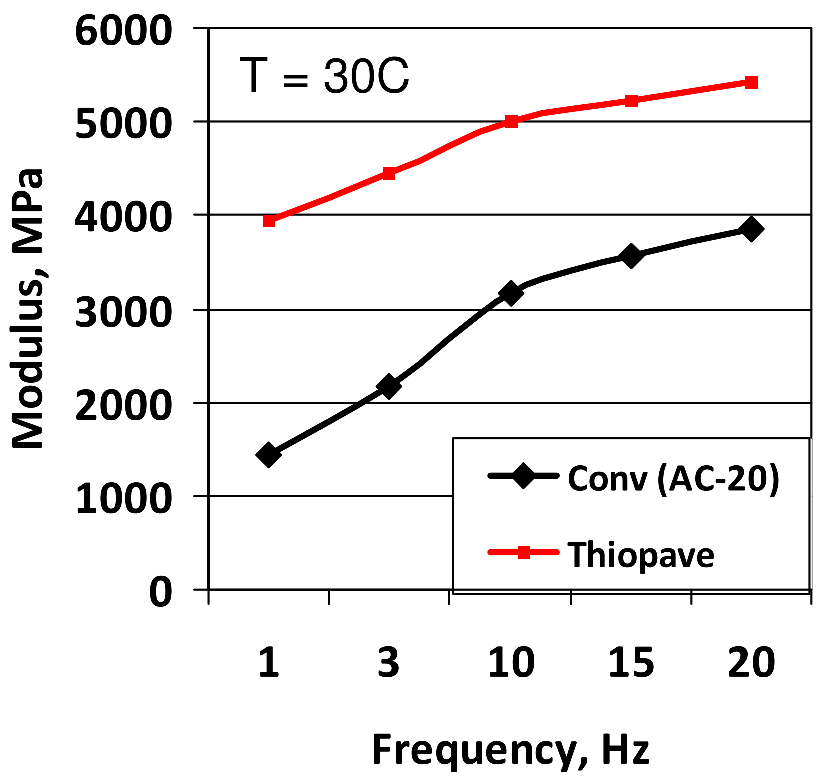
Asphalt Binder: PG 58-28

Temperature Sensitivity



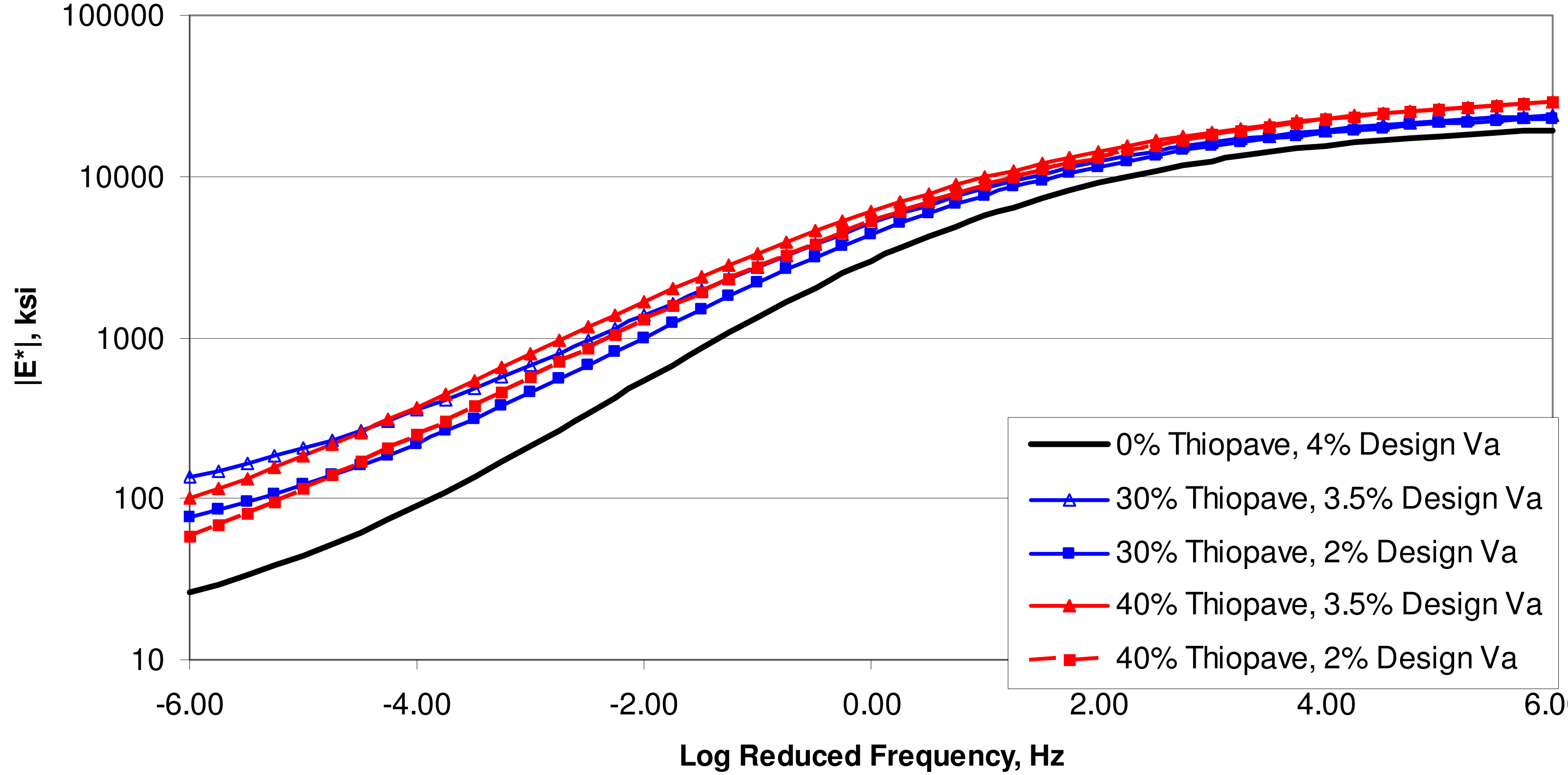
- Thiopave-modified mixtures are *much stiffer* at high temperatures than conventional HMA
- Minimal difference in stiffness at low temperatures
- Conclusion: The stiffness of Thiopave mixtures is less sensitive to temperature changes than conventional HMA

Sensitivity to Loading Time

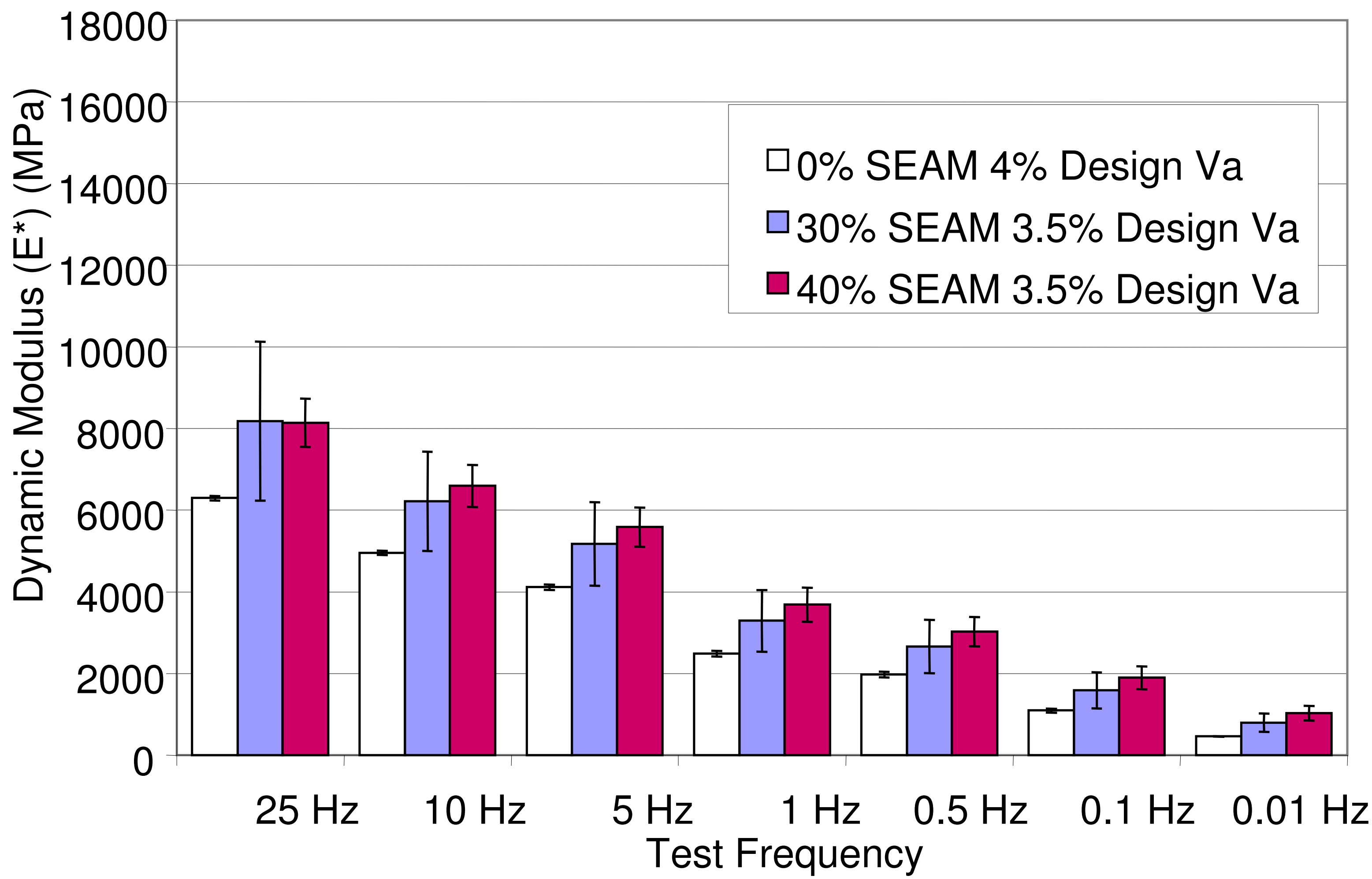


- Greater stiffness at lower speed
  - More rut-resistant
  - Structural improvement
    - Less flexural strain
    - Less vertical compressive strain @ top of subgrade
- Thiopave is less affected by changes in the loading rate than conventional

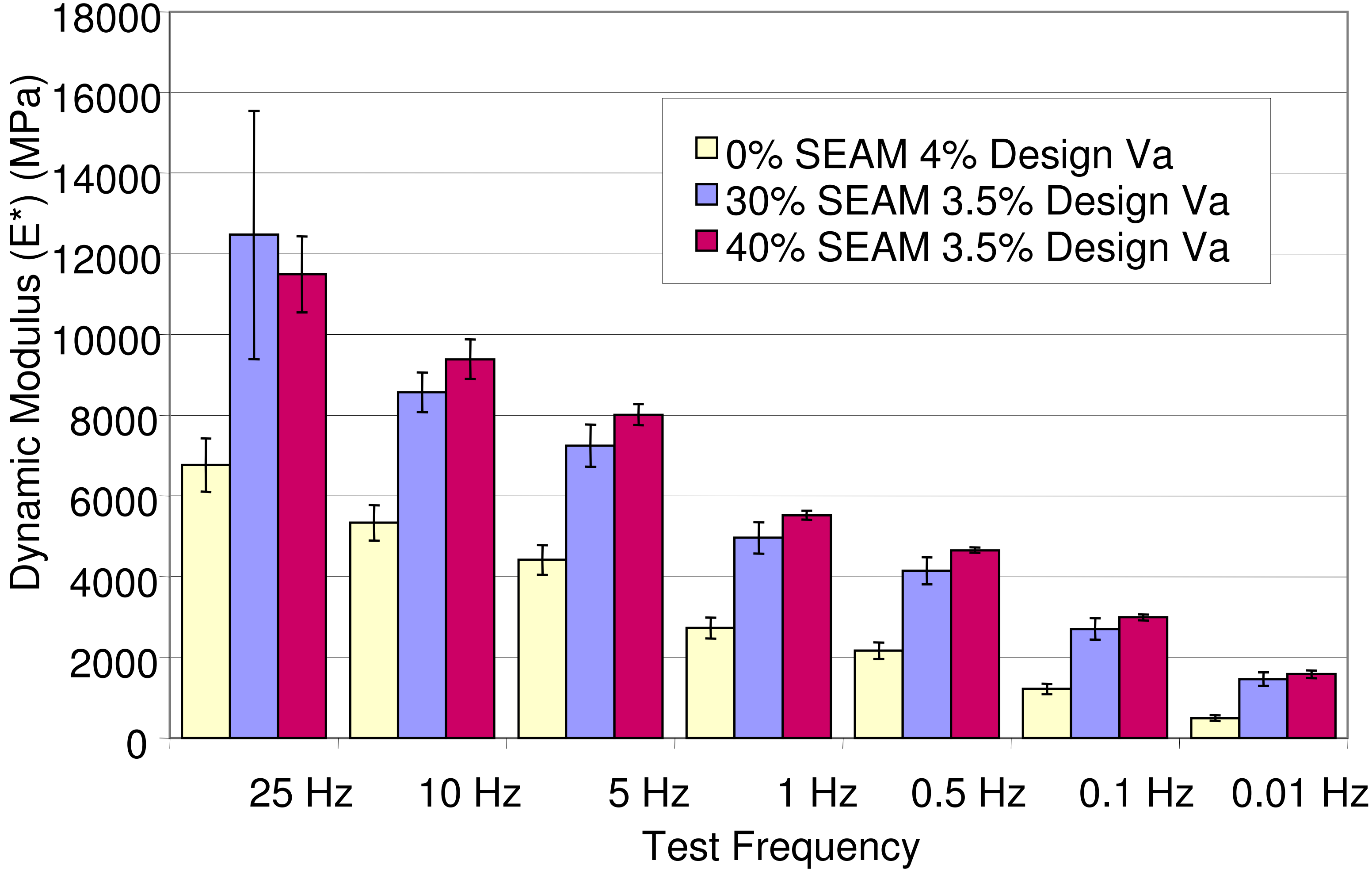
Master Curves (NCAT)



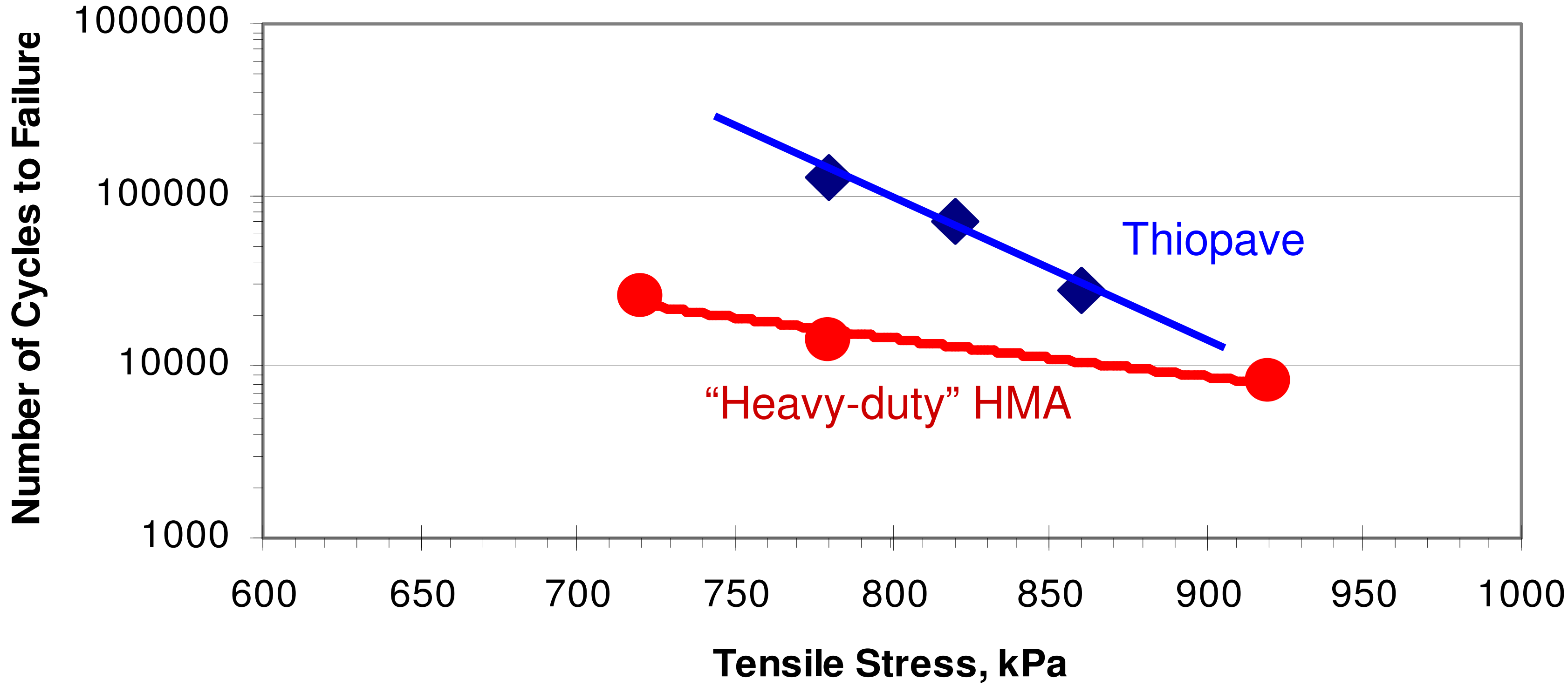
E* vs Frequency, after 1 day



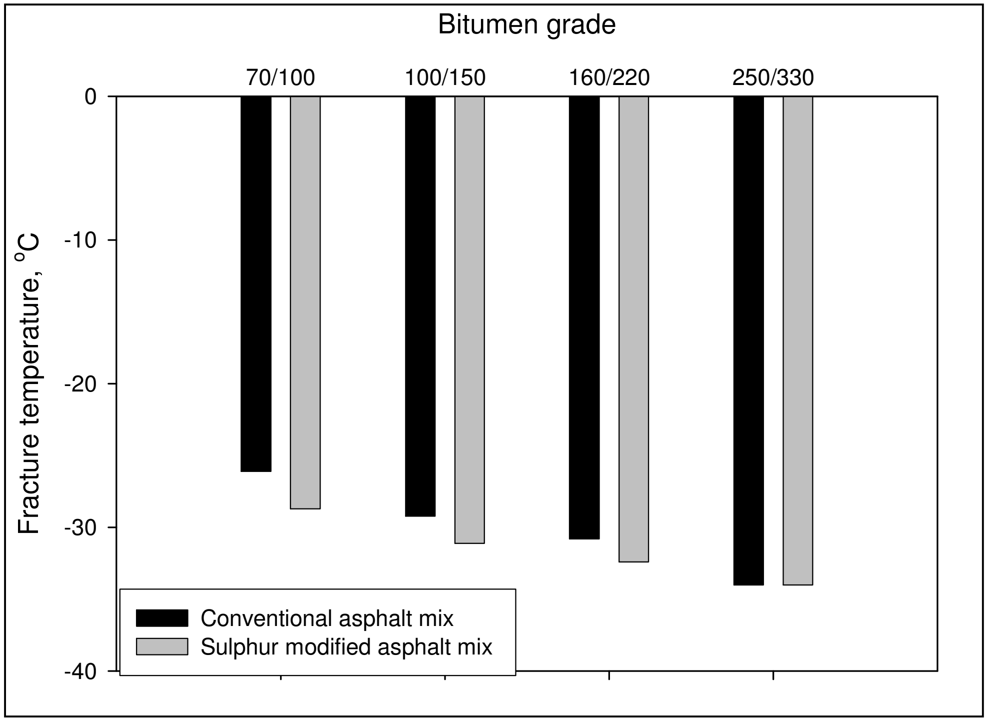
E* vs Frequency, after 14 days

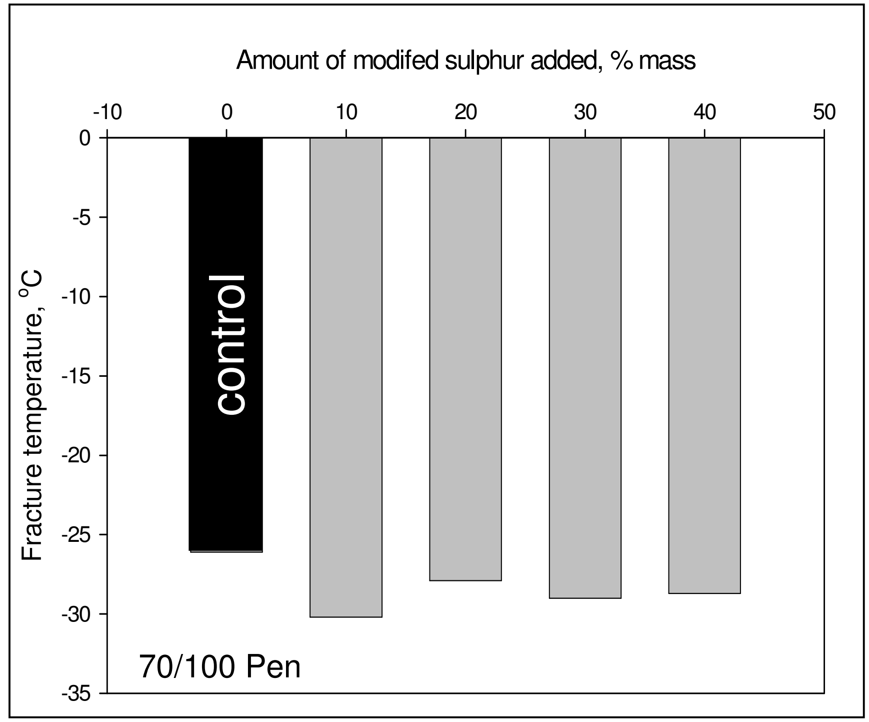


Fatigue Testing, Port of Oakland



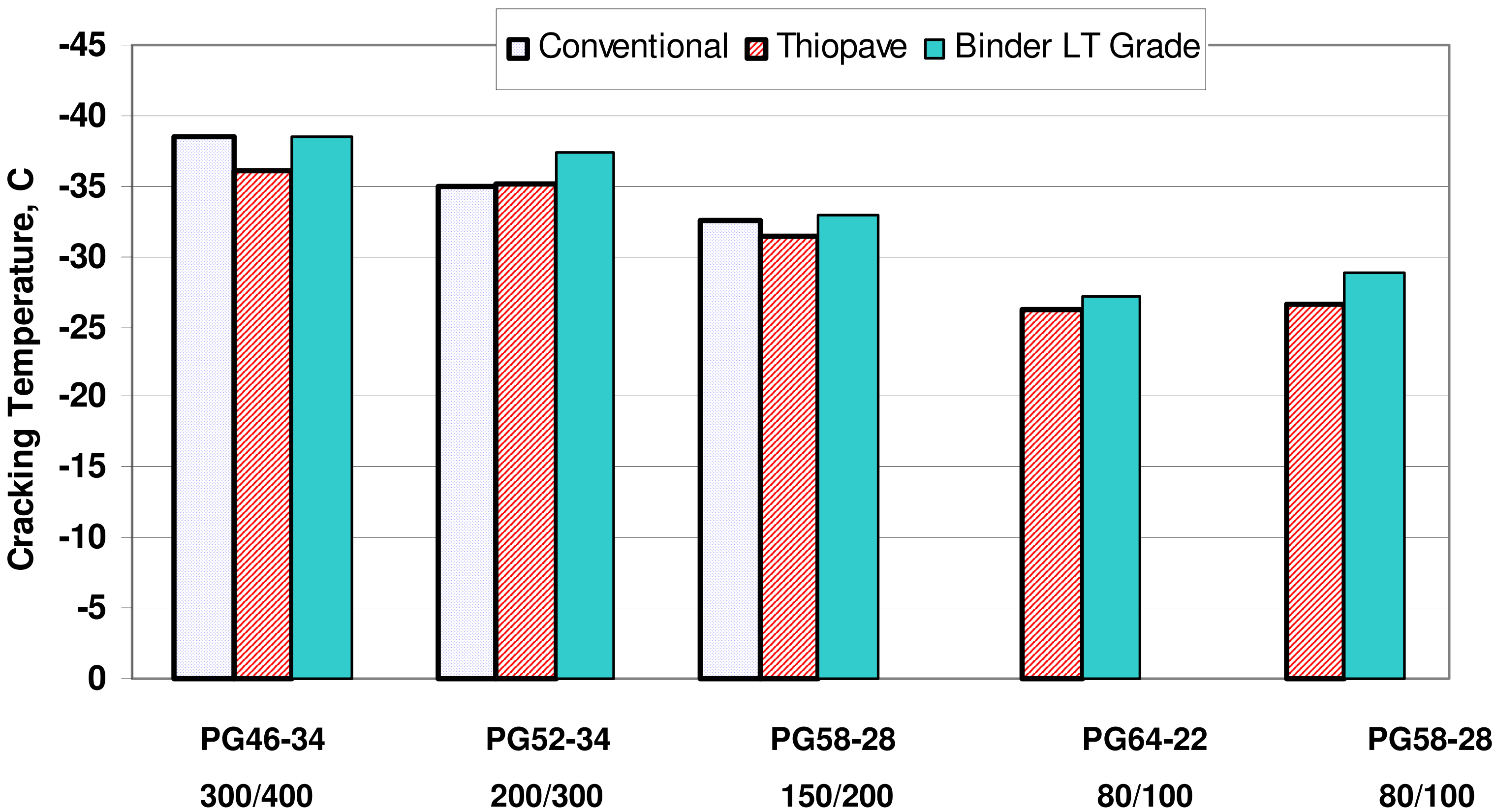
Effect of Thiopave on Thermal Stress Restrained Specimen Tests (TSRST) Results





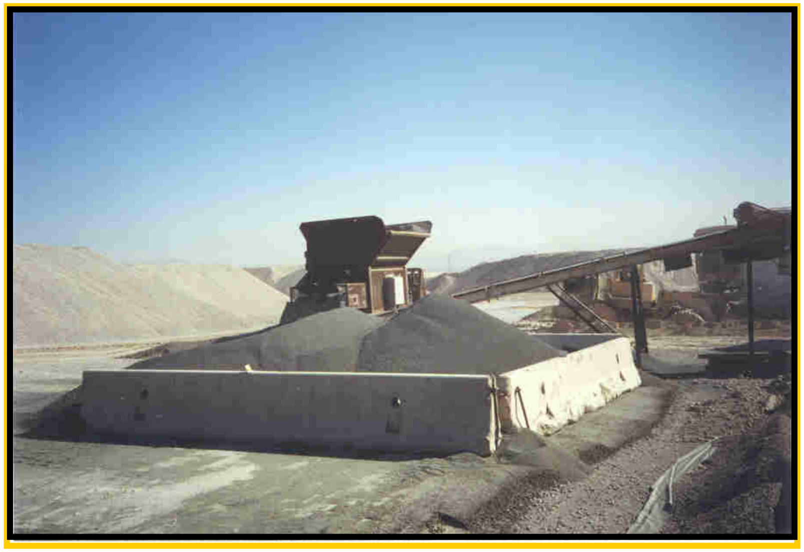
"A Study of the Low-Temperature Properties of Sulphur Extended Asphalt Mixtures" , Strickland, Bouldin and Colange, CTAA 2008

TSRST Comparison



Note: Thiopave Mixtures: 40% Thiopave/60% Bitumen

Production-Feed System



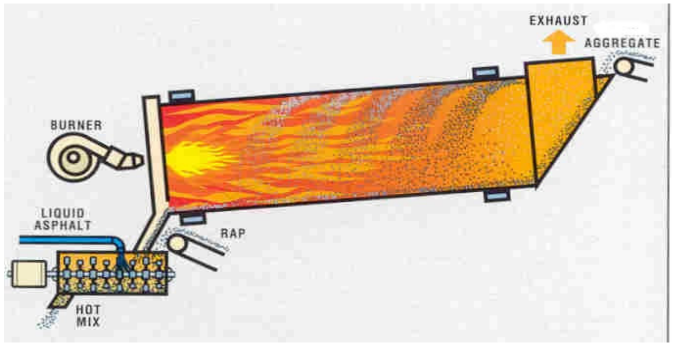
BIN & BELT FEEDER

SILO FEEDER

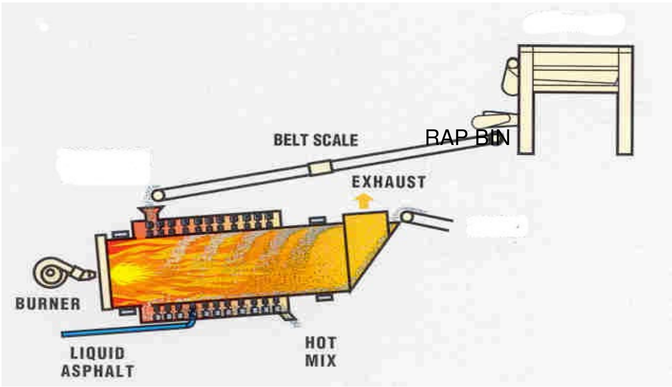
- Developing a pneumatic feed system for Thiopave pastilles
- Best to feed them at/near baghouse fines return

Production

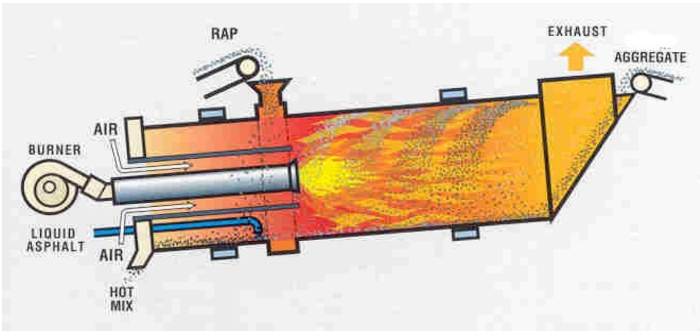
Requires strict temperature control
~ 135C (275F) is ideal



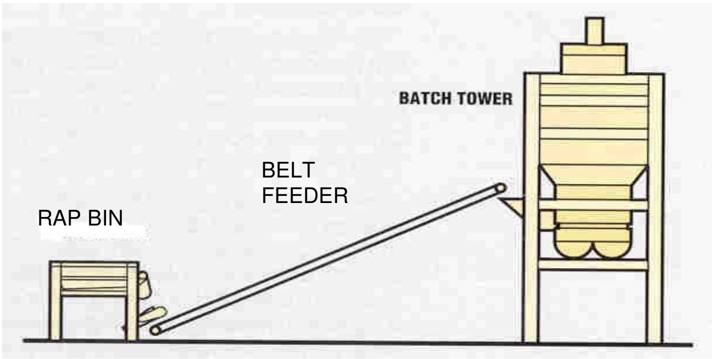
DRUM MIXER WITH SEPARATE COATING MIXER



DOUBLE BARREL DRUM MIXER



COUNTERFLOW DRUM MIXER



BATCH MIXING PLANT WITH RAP FEEDER

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

	ASPHALT PAVER:	H_2S	SO_2
1	ABOVE SCREED (1):	0.9 PPM	0 PPM
2	OPERATOR PANEL (2):	0.1 PPM	0.3 PPM
	AVERAGE LIMIT (2002 TLV):	10 PPM	2 PPM

HS&E - Emissions

Reduced Hydrocarbon Content and Temperature Results in Greatly Reduced VOCs

Date and conditions	**Total VOC ppbv**
Aug 15: Downwind, 5m; Control HMA produced @ 152C	214
Aug 15: Upwind, 5-m; Control HMA @ 152C	257
Aug 16: Breathing zone; Thiopave mix produced @ 140C	98
Aug 16; Downwind, 5m, Thiopave mix produced @ 140C	99

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

Thank you!

Shell
Thiopave
Technologies for Sulphur Enhanced Road Construction

Thiopave®-Sulphur Enhancement for Asphalt Mixtures

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