

A REVIEW OF THE CURRENT SITUATION REGARDING POLYPHOSPHORIC ACID MODIFIED BINDERS

A more or less
personal evaluation
by Gerald Reinke



Mathy Technology and Engineering Services

**IN THE INTEREST OF FULL DISCLOSURE
I HAVE**

- **PERSONAL**
- **PROFESSIONAL**
- **FINANCIAL**

**INTERESTS IN THE SUCCESSFUL UTILIZATION
OF POLYPHOSPHORIC ACID TO MODIFY
BITUMINOUS PAVING MATERIALS**



THERE ARE 2 FACTORS TO CONSIDER WHEN IT COMES TO THE DISCUSSION OF ACID MODIFICATION OF ASPHALTS AND HMA MIXTURES

- 1. THE REACTION OF ASPHALT WITH AN ACID (GENERALLY POLYPHOSPHORIC ACID TODAY) TO YIELD AN IMPROVED PG GRADE RELATIVE TO THE BASE ASPHALT**
- 2. THE USE OF AN ACID REACTANT ALONG WITH A POLYMER MODIFICATION OF THE ASPHALT. GENERALLY TODAY THE POLYMER IS EITHER SBS, SB, OR AN EPOXY BEARING ETHYLENE TERPOLYMER**

VIEW (of some) FROM
OUTSIDE THE INDUSTRY

ACID MODIFICATION OF
ASPHALT

THE SPAWN OF SATAN



SOME POINTS TO PONDER GOING FORWARD

- 1. ACID MODIFICATION HAS BEEN USED IN LOUISIANA FOR ABOUT 20 YEARS TO MAKE AC-30 AND AC-40 WITH SOME BINDERS**
- 2. BEGINNING IN 1992/1993 ACID ONLY MODIFICATION AND POLYMER + PPA MODIFICATION HAS GROWN IN USAGE ACROSS THE US**
 - a) AT THIS POINT SUPPLIERS IN ALL PARTS OF THE US USE THIS PROCESS**
 - b) I CONSERVATIVELY ESTIMATE THAT IN THAT TIME PERIOD AT LEAST 3,000,000 TONS OF BINDER CONTAINING PPA HAVE BEEN USED. THIS EQUALS ABOUT 51,000,000 TONS OF MIX**
- 3. GIVEN THESE QUANTITIES IF THERE ARE WHOLESALE PROBLEMS WITH THIS ADDITIVE DON'T YOU THINK WE ALL WOULD BE AWARE OF THEM?**



BACKGROUND PREPARATION FOR THIS TALK

1. I THOUGHT ABOUT CONDUCTING ANOTHER SET OF TESTS TO SHOW THE BEHAVIOR OF PPA MODIFIED BITUMEN & MIXES—
 - A. RAPIDLY DISCARDED IDEA—HOW MUCH DATA IS ENOUGH?
 - B. MORE DATA WON'T CONVINCE THE UNCONVINCABLE
 - C. MORE DATA IS ONLY PREACHING TO THE CHOIR FOR THOSE WHO USE THE PPA
2. AT THIS POINT IN TIME WE ARE NOT



WE ARE DEALING WITH SOMETHING AKIN TO A PERSONAL BELIEF SYSTEM

➤ **POLITICS**

➤ **RELIGION**

➤ **WHAT ARE “YOUR” VIEWS ON ACID
MODIFIED ASPHALT?**

SO WHAT'S GOING ON!

1. THE INDUSTRY GOT TOO SMART FOR ITS OWN GOOD

A. INDIVIDUALS & COMPANIES THOUGHT THEY HAD A COMPETITIVE ADVANTAGE OVER THE NEXT GUY

B. SOME CONCERN THAT THE PRODUCT WOULD NOT BE ACCEPTED BECAUSE IT WAS NOT POLYMER (OR ALLOWED LESS POLYMER TO BE USED), YET YIELDED EXPANDED PG GRADES

a) TREATMENT OF OXIDIZED ASPHALT SET THE STAGE FOR CONCERN



2. AGENCIES GOT WIND OF THE USE OF ACID AND
 - A. ASSUMED IT HAD TO BE BAD, BECAUSE AFTER ALL IT WAS ACID AND NO ONE REALLY WANTED TO TALK TO THEM ABOUT IT
 - B. RAPIDLY CONDUCTED TESTS BY SOME AGENCIES AND BY SOME COMPANIES LED TO THE OBVIOUS CONCLUSION:

**YOU MIX AN ACID & A BASE
TOGETHER AND THEY WILL
REACT! IN THE LABORATORY**



3. INDUSTRY CAME LATE TO THE (PUBLIC) DEFENSE OF ACID MODIFIED ASPHALT

- A. RESPONSIBLE SUPPLIERS AND VENDORS HAD BEEN EVALUATING THE MIX PERFORMANCE IMPACT OF ACID MODIFICATION FROM AT LEAST 1993.
- B. INFORMATION KEPT INTERNAL (TRADE SECRETS, INTELLECTUAL PROPERTY, COMPETITIVE ADVANTAGE, ETC)
- C. CONTRARY TO POPULAR MISCONCEPTION SUPPLIERS TO THIS INDUSTRY AREN'T TRYING TO “SLIP SOMETHING BY”. WE ALL HAVE TO LIVE WITH THE RESULTS OF OUR DECISIONS—BE THEY BUSINESS OR TECHNICAL



- 4. SOME STATES DECIDED TO HANDLE THE PROBLEM FOR THE ASPHALT PRODUCTION & SUPPLY INDUSTRY
 - A. ARMED WITH A LITTLE KNOWLEDGE AND A LOT OF FEAR SOME STATES OUTRIGHT BANNED THE USE OF ACID MODIFIED ASPHALT AND IN SOME CASES THE USE OF ACID AS CO-REACTANT WITH POLYMERS
 - B. OTHERS ARE WAITING TO DECIDE, BUT EVERYONE IS CONCERNED. BUT WHY?

JOB FAILURES

❑ WHERE ARE THESE FAILURES?

❑ HAS THE FORENSIC WORK BEEN PERFORMED TO VERIFY ACID AS THE CAUSE?

✓ IT IS AN UNFORTUNATE FACT, BUT SOME BITUMINOUS JOBS FAIL—EVEN THOSE PERFORMED WITH MATERIALS HAVING A LONG HISTORY OF USAGE

❑ HAVE THE CONTRACTORS AND SUPPLIERS BEEN INVOLVED IN THE INVESTIGATIONS? THESE PEOPLE KNOW MORE ABOUT THE NITTY GRITTY DETAILS THAN ANYONE ELSE



FEAR OF JOB FAILURES

❑ FEAR OF STRIPPING

- FEAR OF NEUTRALIZATION BY LIME OR AMINE ADDITIVES

- FEAR OF INCOMPATIBILITY WITH SOME AGGREGATES

❑ FEAR OF PREMATURE AGING

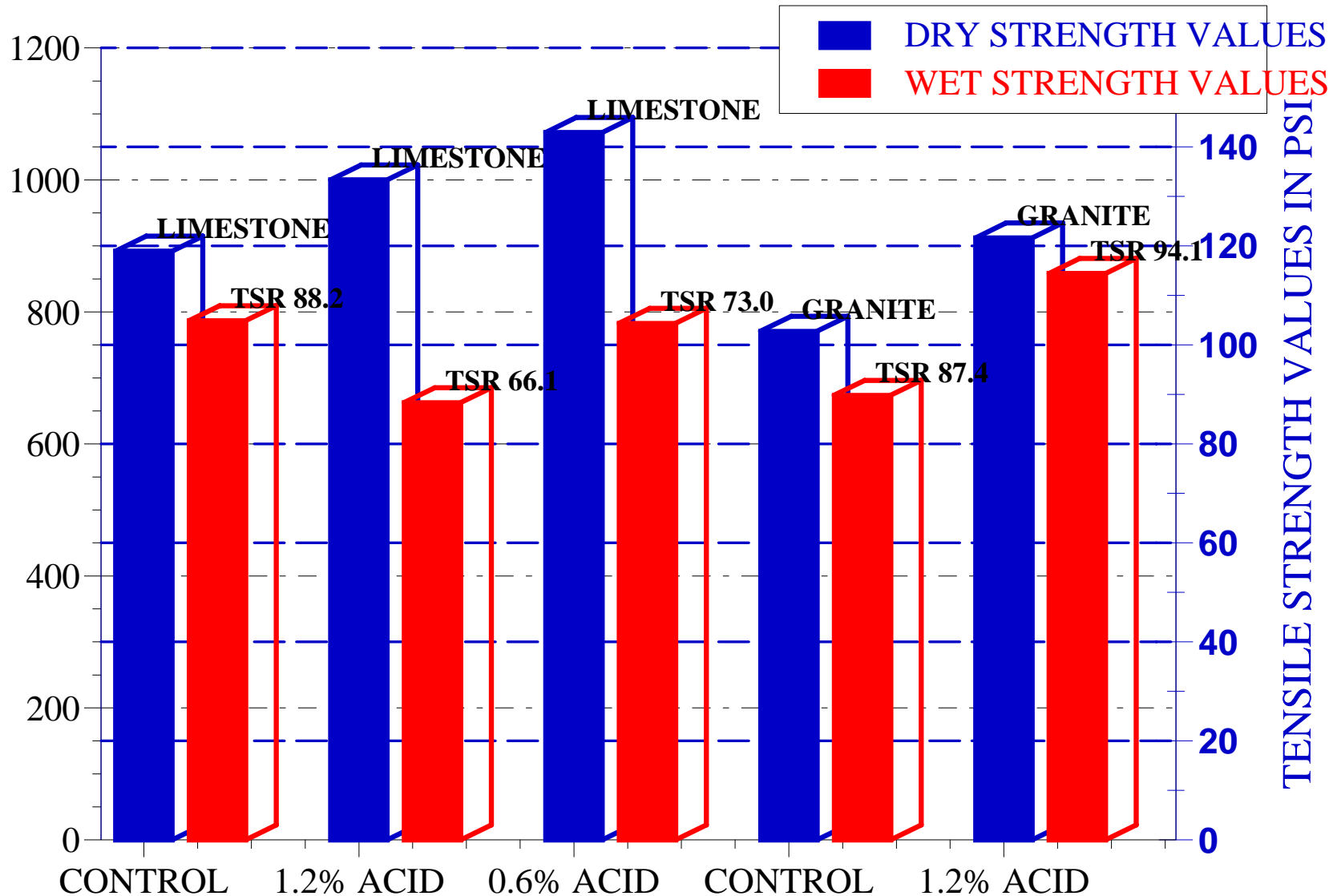
- FEAR OF THERMAL CRACKING

- FEAR OF FATIGUE FAILURES

N

TENSILE STRENGTH TEST RESULTS FOR SOURCE C 67-22 ID SOURCE C 67-22 + 1.2% OR 0.6% POLYPHOSPHORIC ACID USING LIMESTONE AND GRANITE MIXES

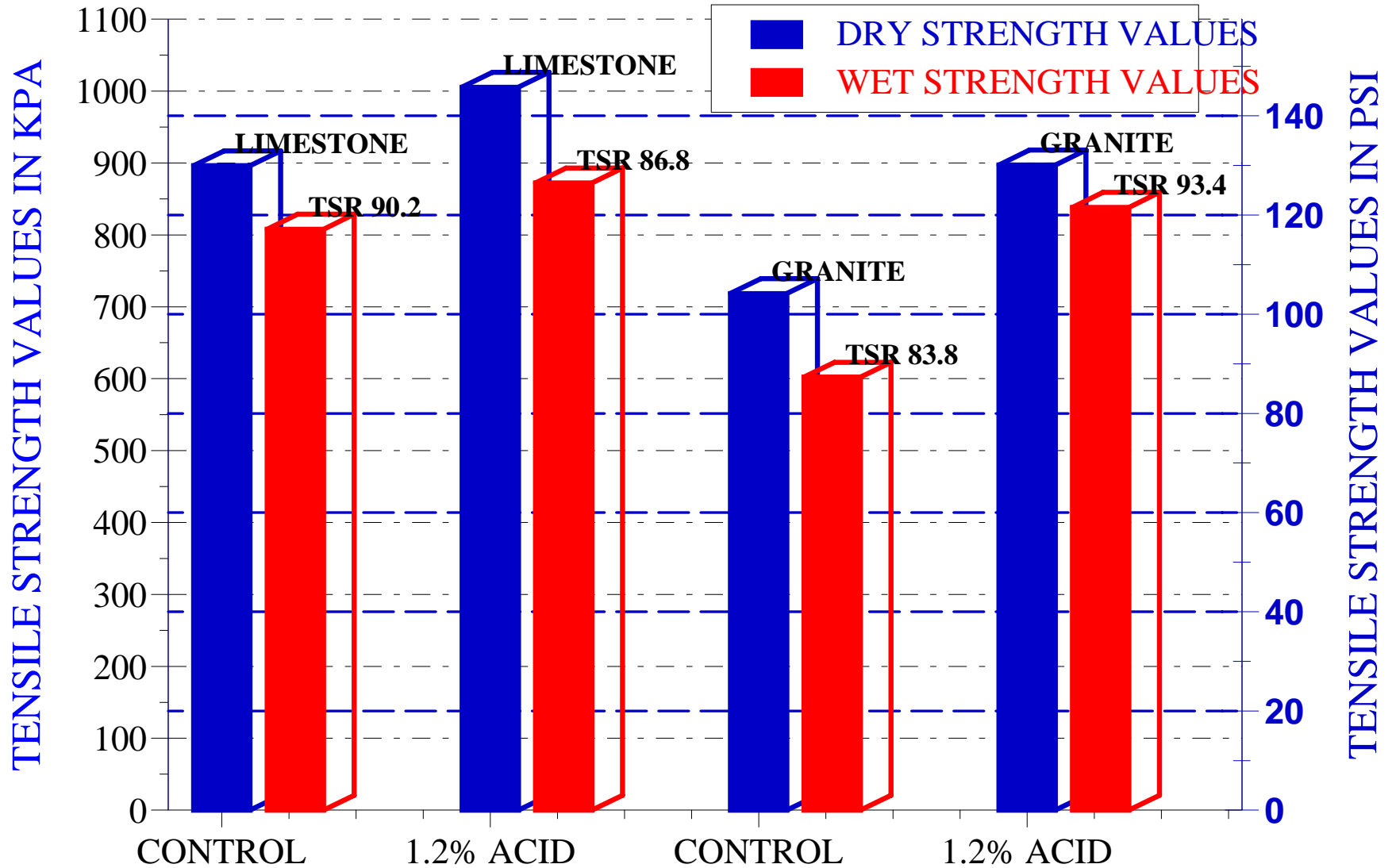
TENSILE STRENGTH VALUES IN KPA



TENSILE STRENGTH VALUES IN PSI

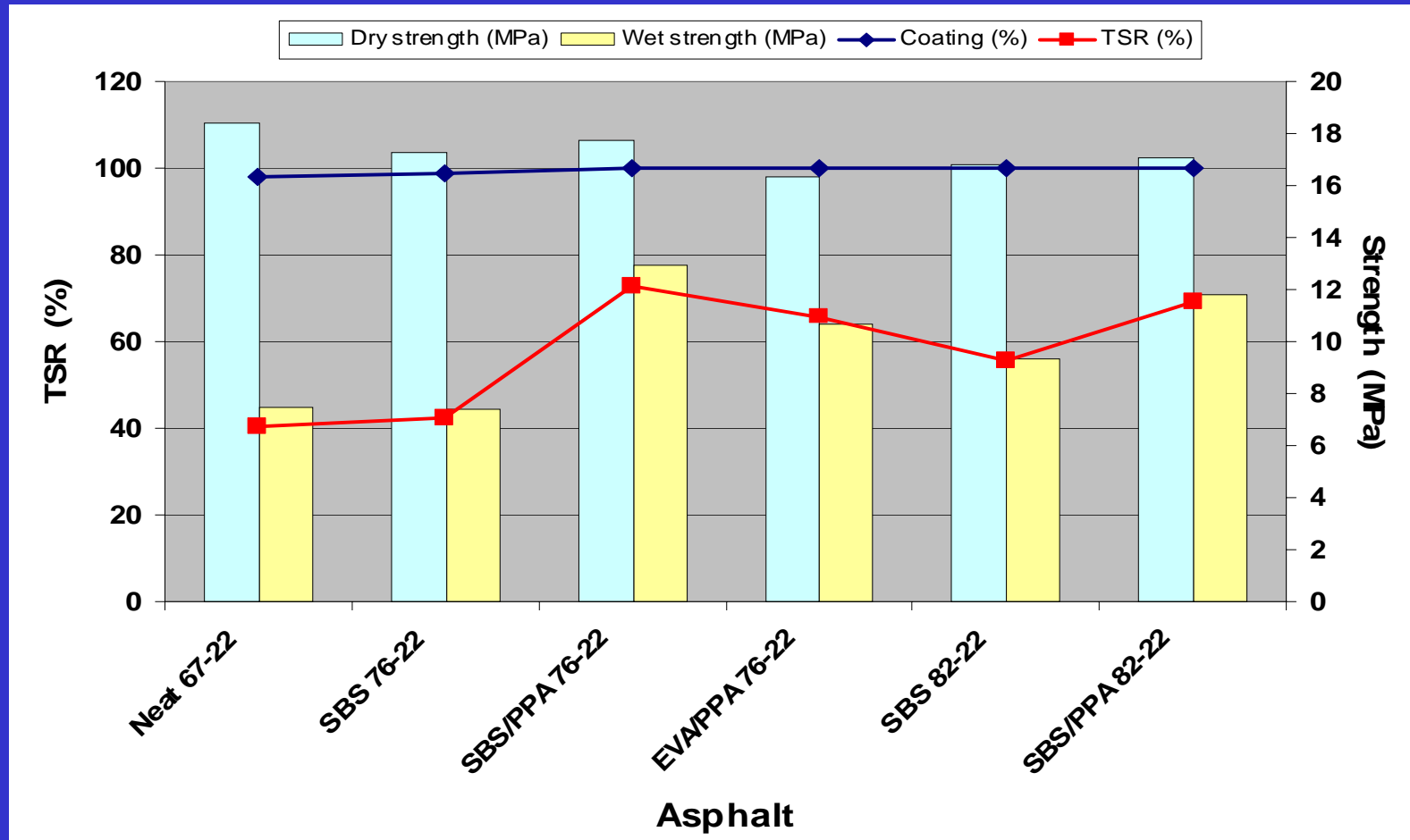


**TENSILE STRENGTH TEST RESULTS FOR SOURCE B 64-22
AND SOURCE B 64-22 + 1.2% POLYPHOSPHORIC ACID
USING LIMESTONE AND GRANITE MIXES**

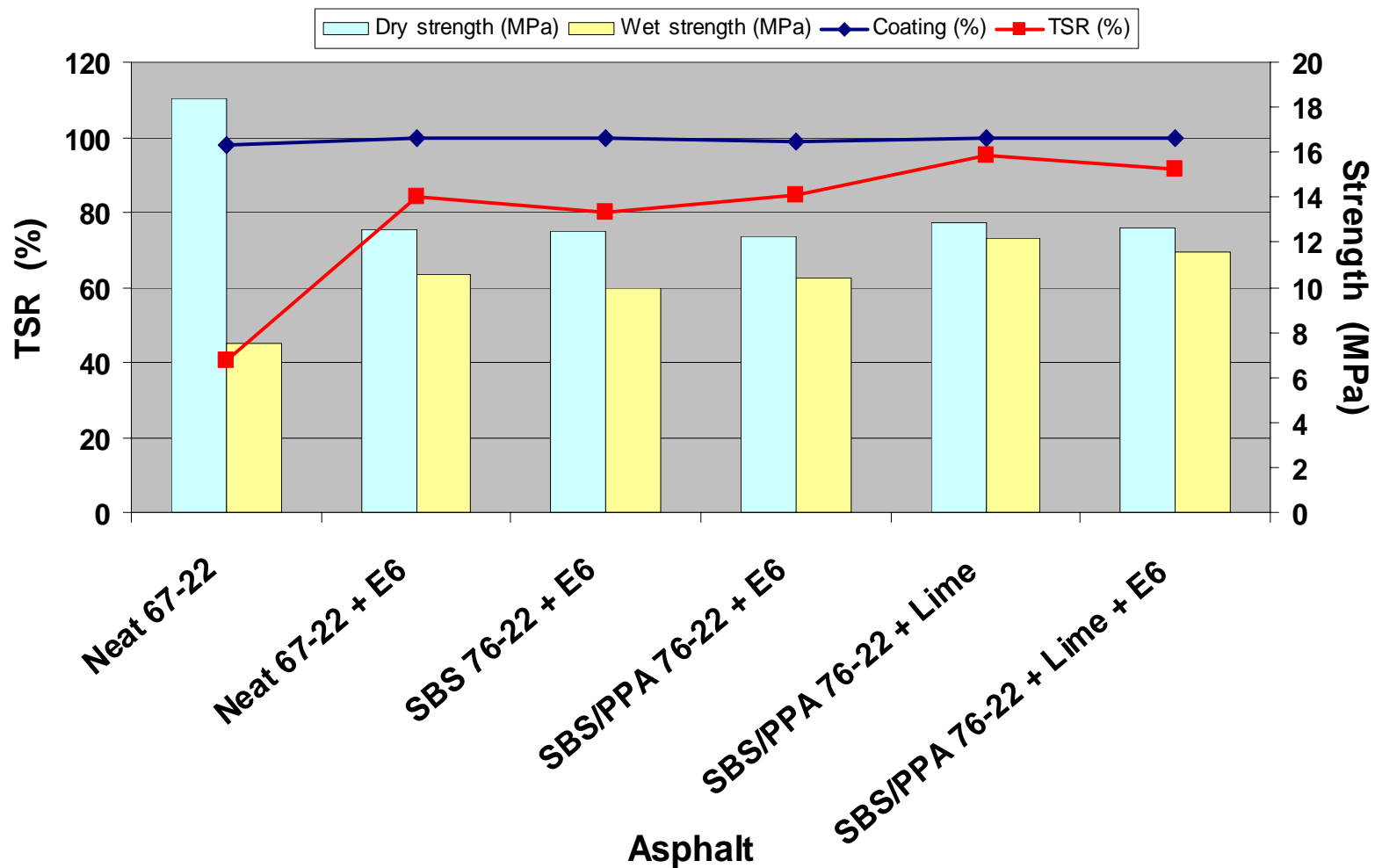


Moisture Resistance (TSR)

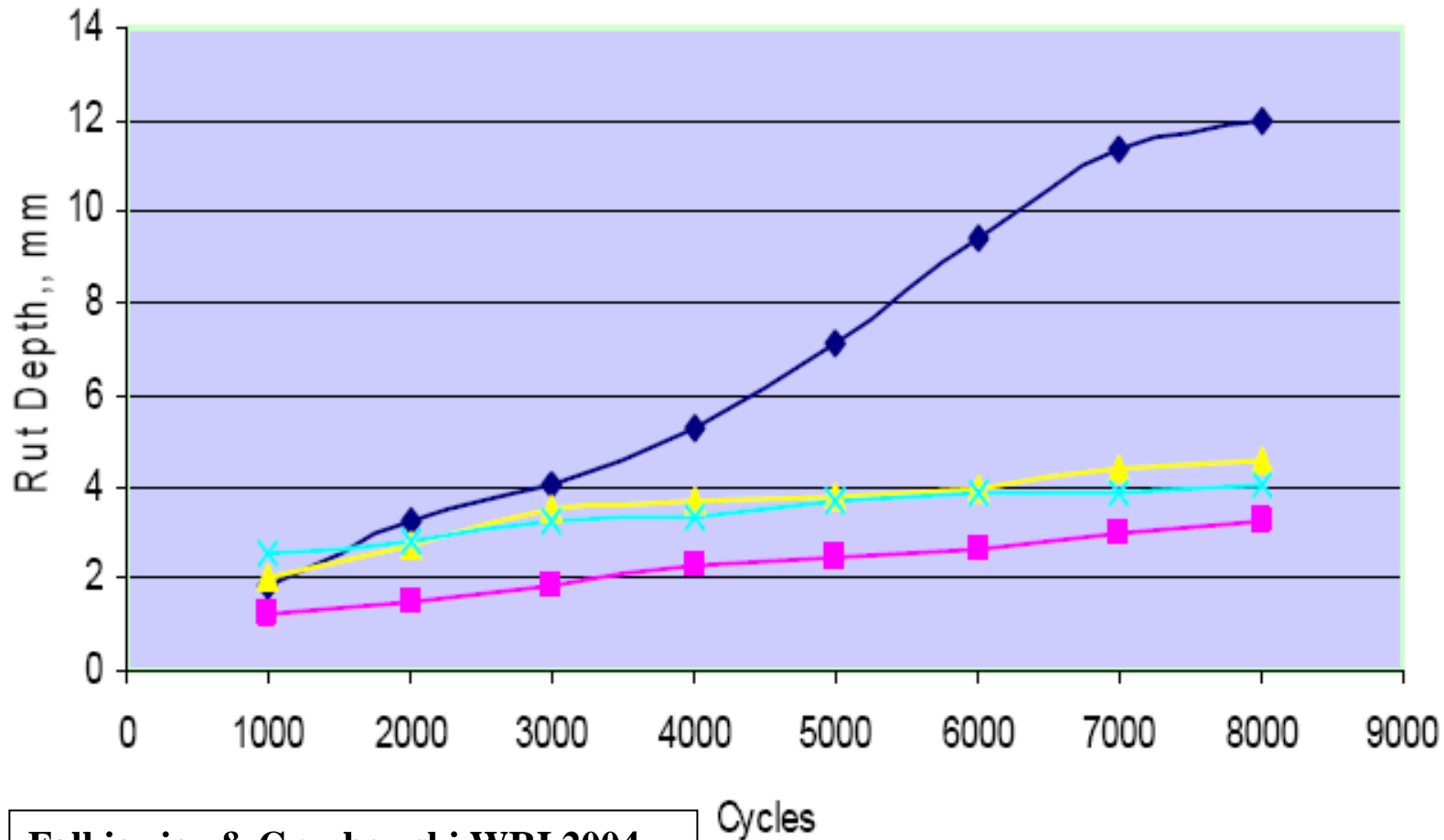
Venezuelan Asphalt/Granite Agg.



Moisture Resistance (TSR) Venezuelan Asphalt/Granite Agg. W/Lime and Polyamine



Hamburg Rut Depth, 50 deg C



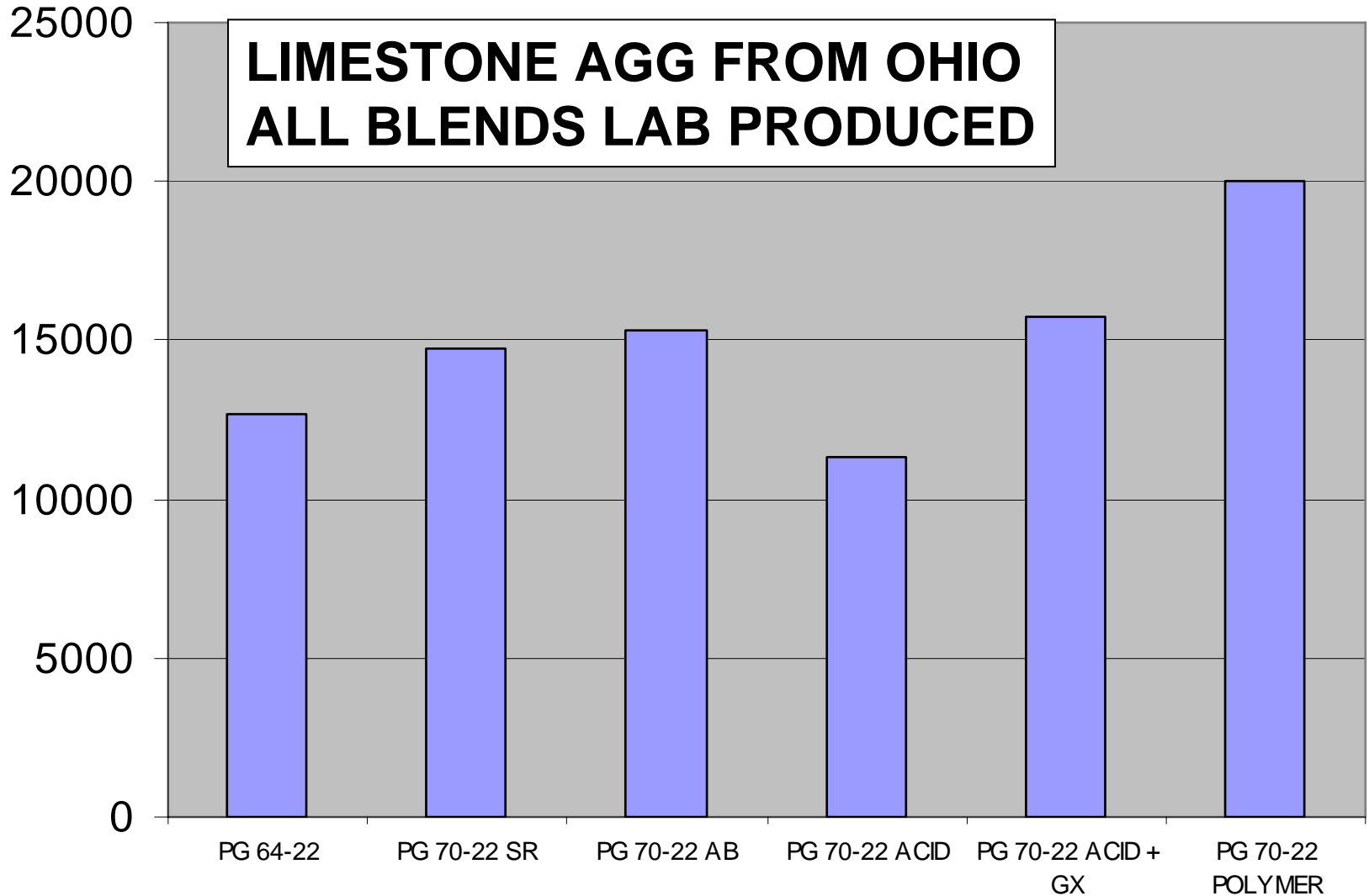
- Control, C 67-22
- C+0.5% 115+ 2% Lime
- C+0.5% 115 + 0.5% LAS 2
- C+2.0% Lime

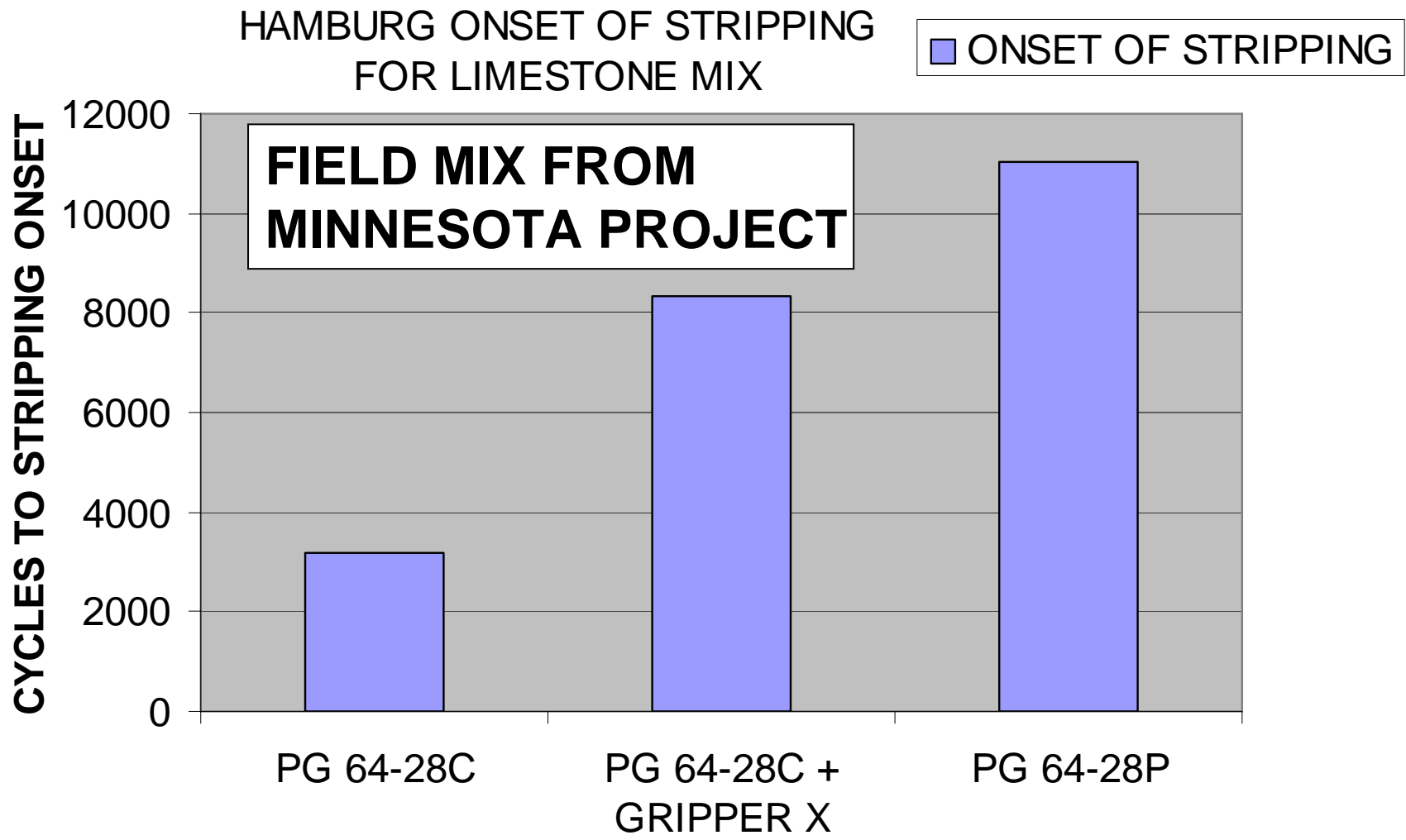
HAMBURG RUT TEST CYCLES TO STRIPPING ONSET

■ CYCLES TO
STRIPPING ONSET

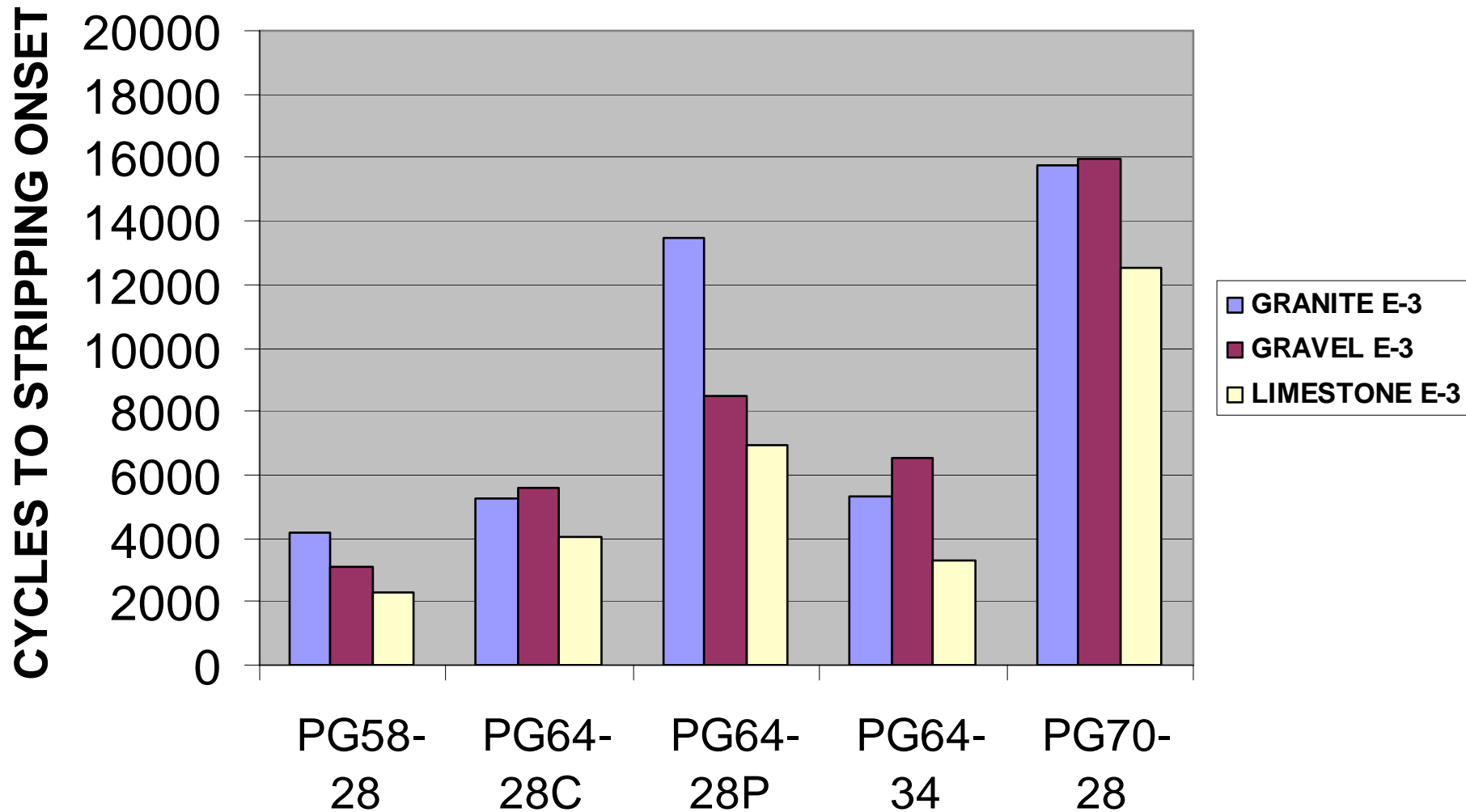
HAMBURG CYCLES TO STRIPPING

**LIMESTONE AGG FROM OHIO
ALL BLENDS LAB PRODUCED**

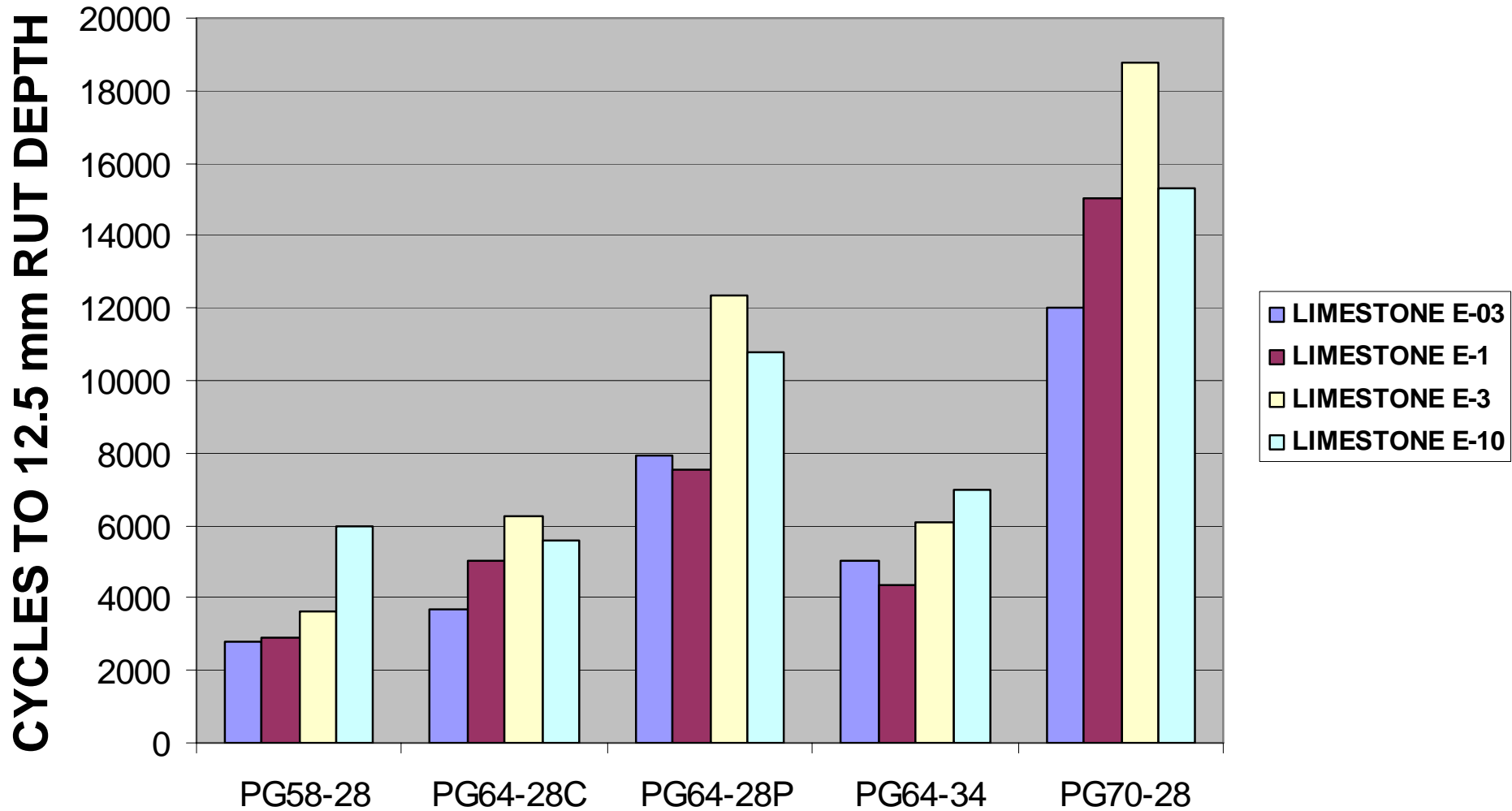




CYCLES TO STRIPPING ONSET FOR E-3 MIXES

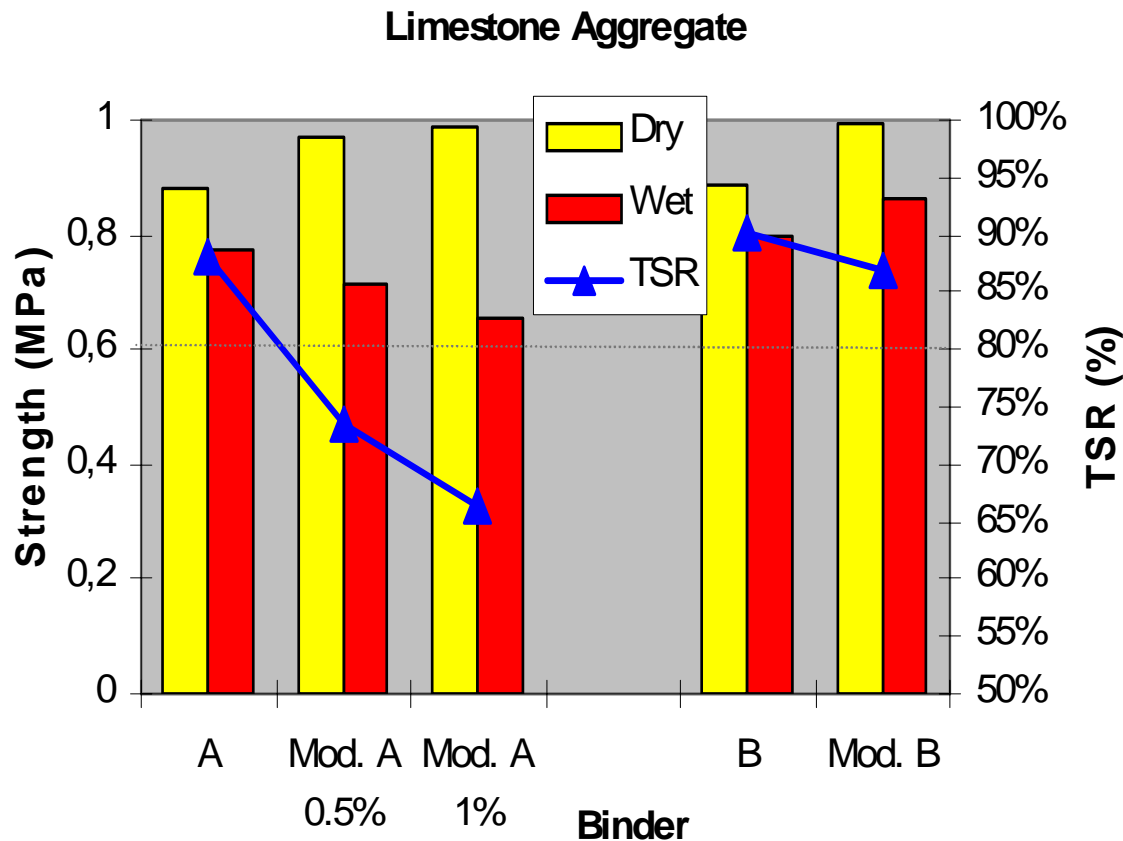


CYCLES TO 12.5 mm for LIMESTONE MIXES



Depending on the nature of the asphalt and the aggregates , antistrip additive could be required in combination with PPA

TSR RESULTS : Limestone Aggregates (Medary)



A : CITGO

B : BP

Consistent results with Boiling Tests observations

In case of Naphtenic

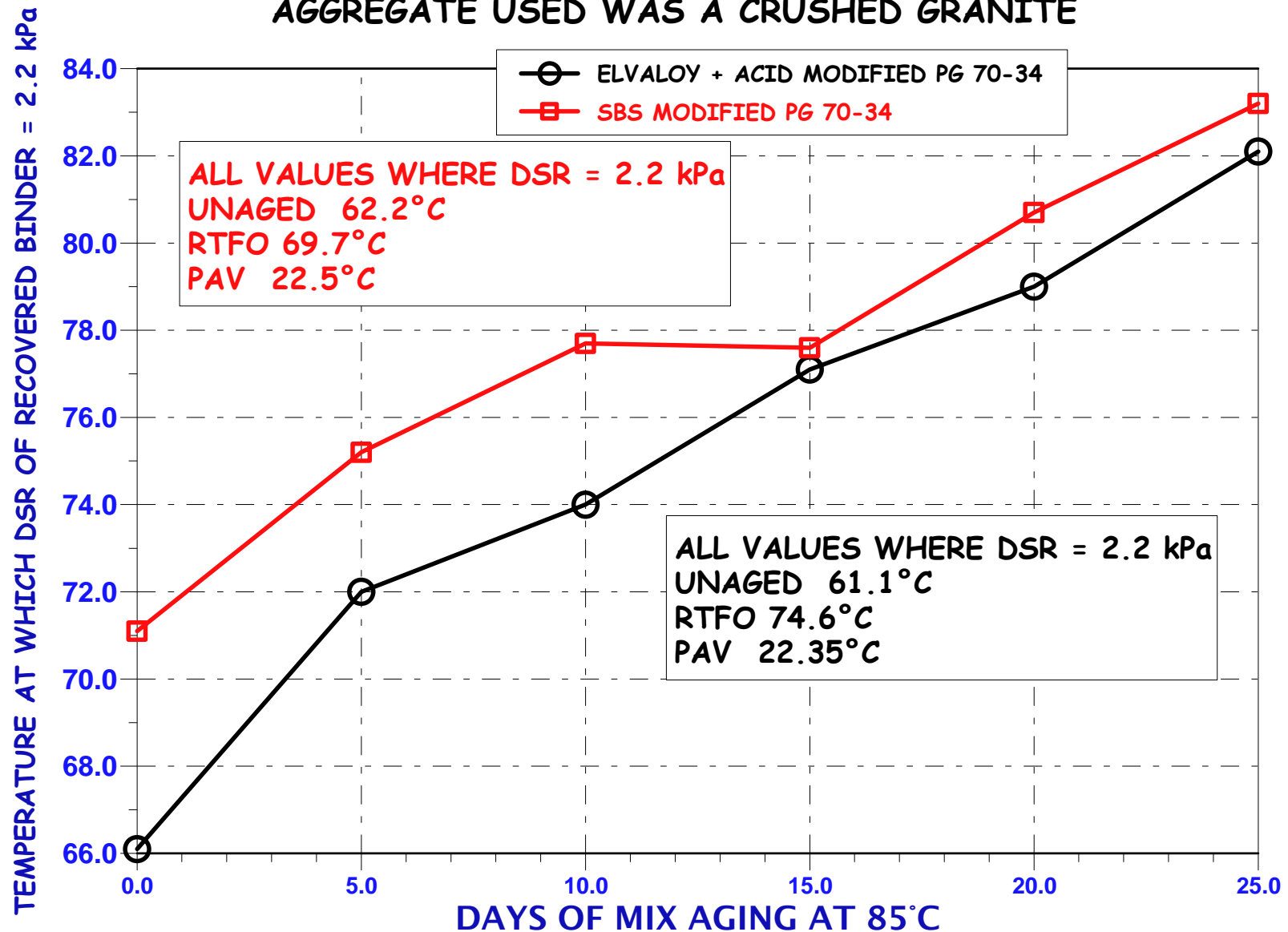
- Higher moisture sensitivity in presence of PPA is observed

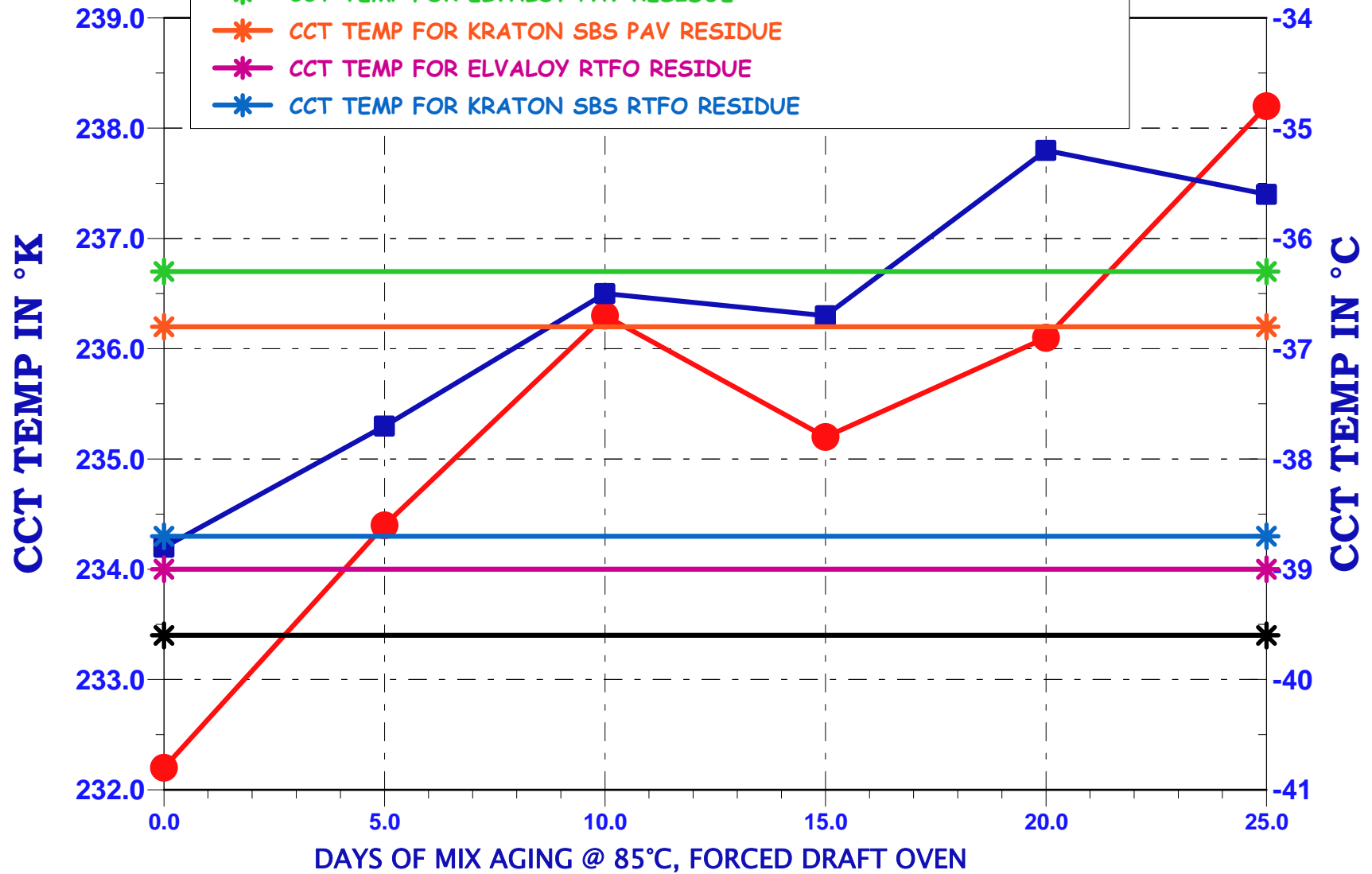
A compatible antstrip is requested

In case of Paraffinic :

- Dry and wet sample tension strength are improved in presence of PPA, but the improvement is higher in dry condition than for the wet one

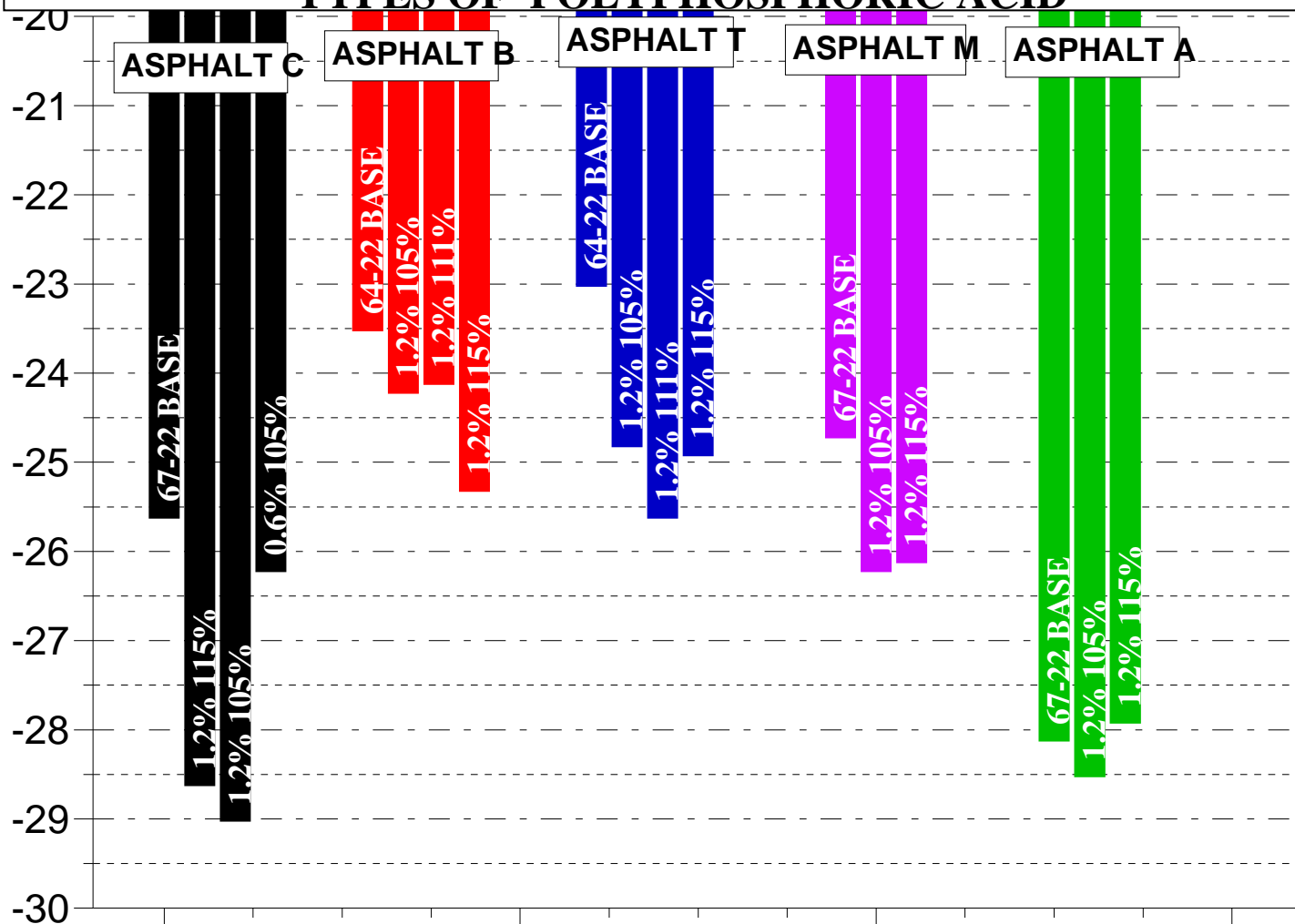
AGING COMPARISON OF SBS WITHOUT ACID &
ELVALOY WITH ACID CATALYST
AGGREGATE USED WAS A CRUSHED GRANITE



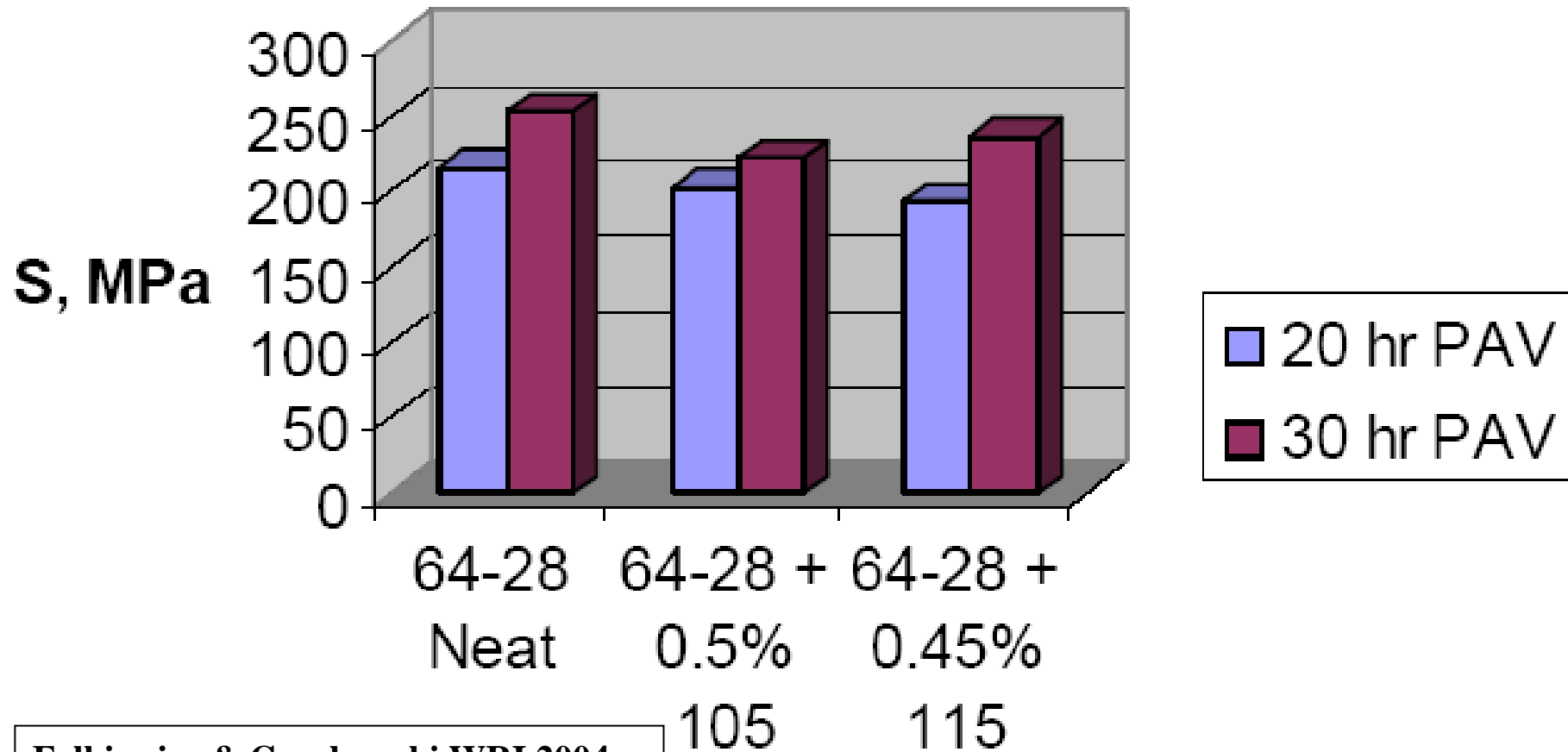


IMPACT ON CRITICAL CRACKING TEMPERATURE OF BINDER

ADDITION OF 1.2% (0.6% FOR ONE SAMPLE OF DIFFERENT TYPES OF POLYPHOSPHORIC ACID

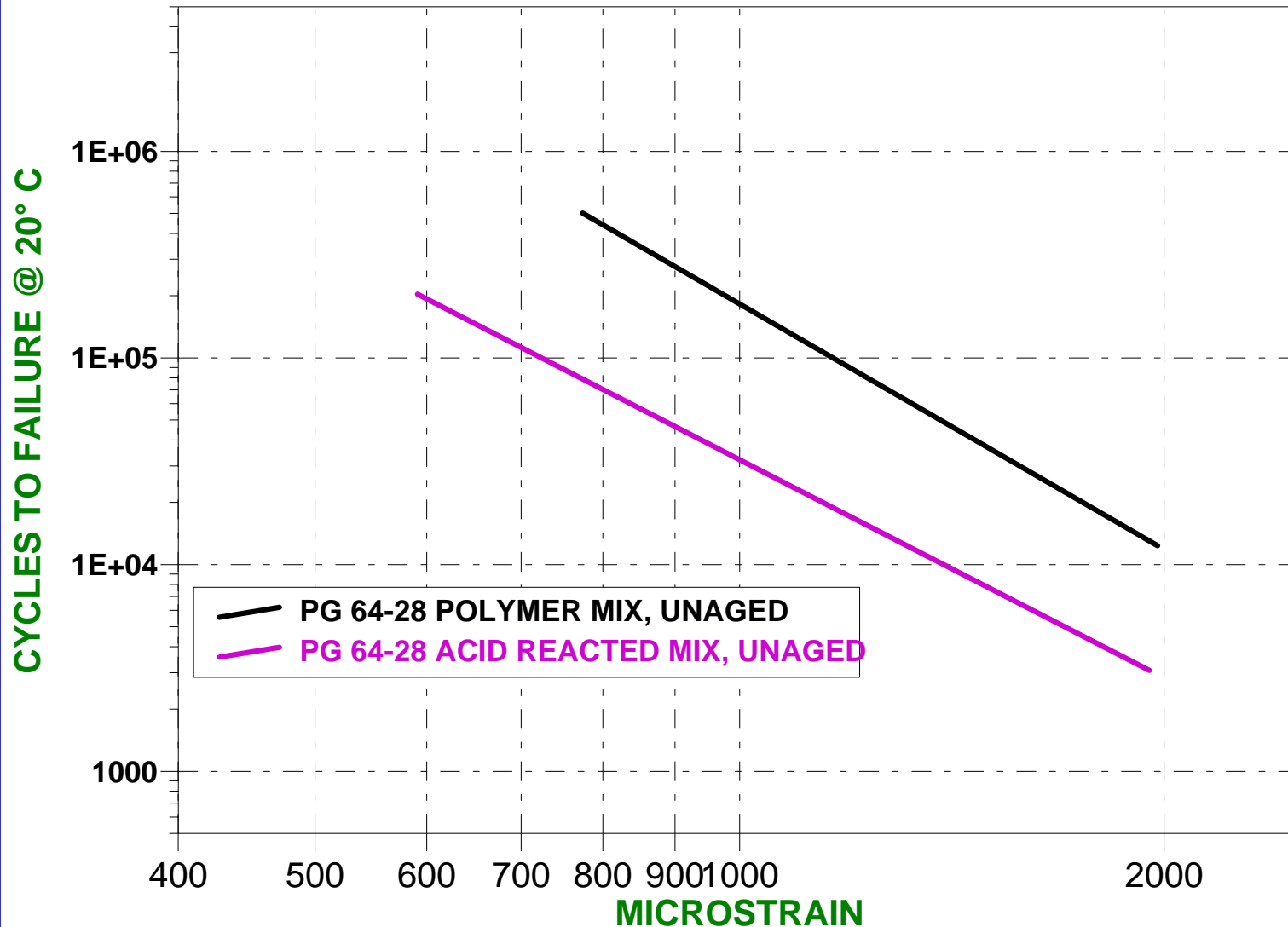


Extended Oxidative Aging - Asphalt B



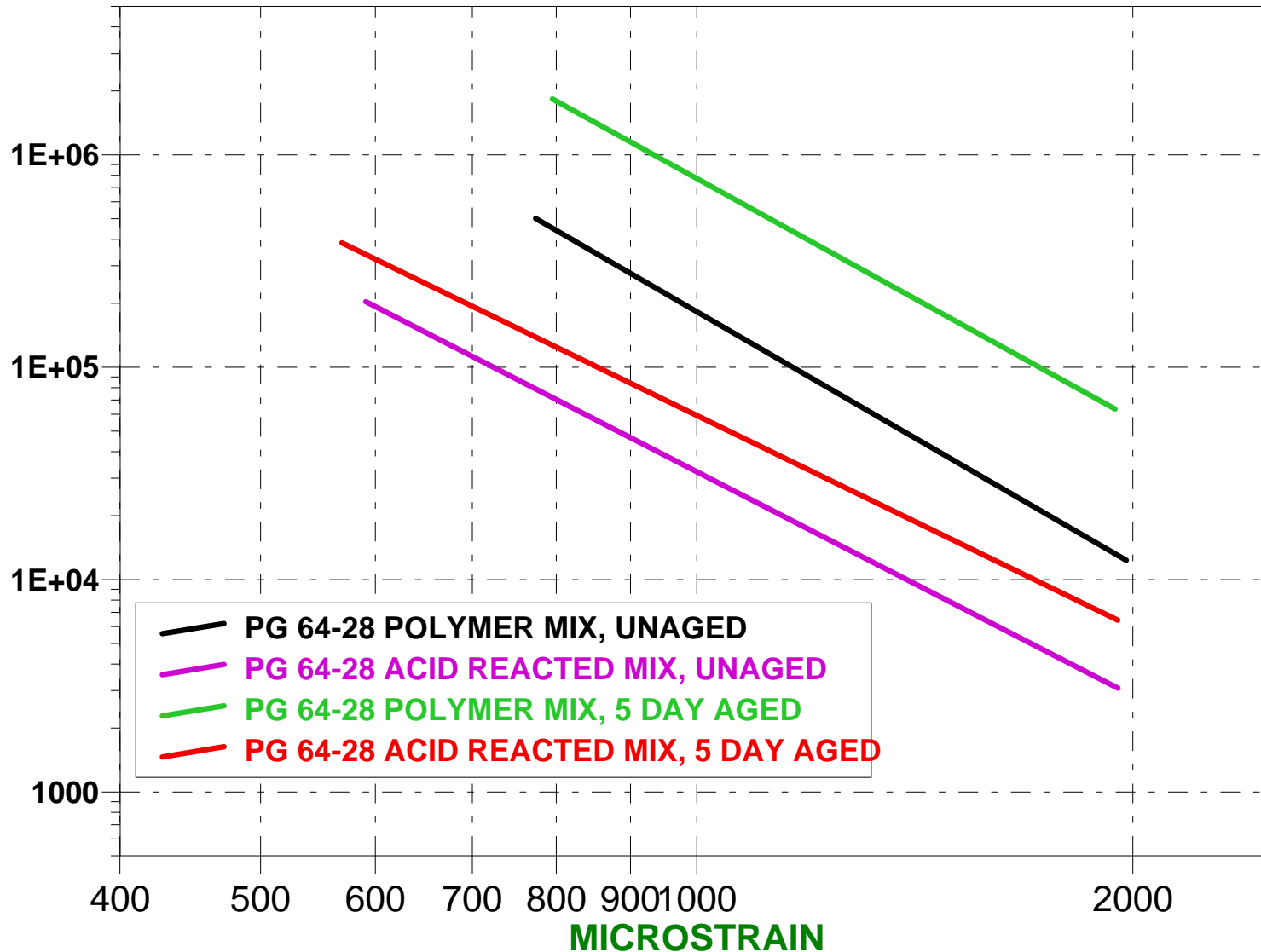
Falkiewicz & Grzybowski WRI 2004

COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED

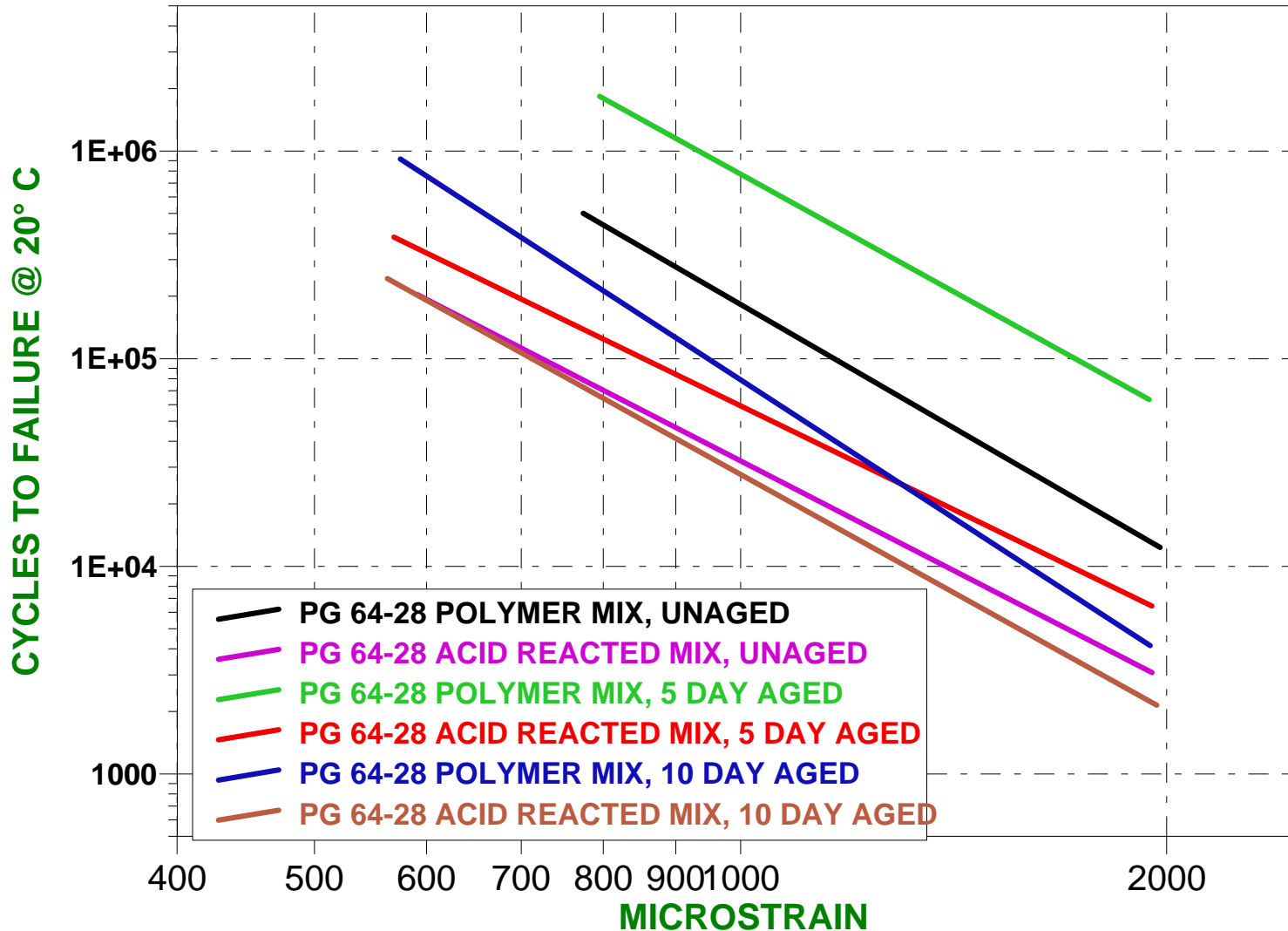


COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED

CYCLES TO FAILURE @ 20° C



COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED



INFORMATION AVAILABLE

1. BISHARA S.W., KING G. N., MAHONEY D., McREYNOLDS R.L, "Modification of binder with acid. Advantages and Disadvantages", Presented at Transportation Research Board meeting January 2001
2. KING Gayle, BISHARA S.W., FAGER G., "Acid/Base Chemistry for Asphalt Modification", Proceedings of the Association of Asphalt Paving Technologists, Vol. Xx, 2002

1 to 2% of 85% phosphoric acid was used to modify various binders

Amines caused reduction in T_{high} of binders

TSR, APA and Hamburg tests were performed on different mixtures, although not all tests were performed on all mixtures. Therefore direct comparisons between moisture sensitivity tests and different binder treatments could not be made on all mixtures. **High amount of acid increased moisture sensitivity of mixtures**



INFORMATION AVAILABLE

3. Ho S. M. S., Zanzotto L., MaCloed D., "Impact of Different Types of Modification on Low-Temperature Tensile Strength and Tcritical of Asphalt Binders", *Transportation Research Record*, N 1810, 2002.
4. Ho S. M. S., Zanzotto L., MaCloed D., "Impact of Chemical Modification on Composition and Properties of Asphalt Binders", 46th Annual Conference of the Canadian Technical Asphalt Association, Vol. XLVI, 2001

PPA modification partially or substantially reversible in the presence of lime directly dependent upon the amount of lime added to the PPA modified binder. Up to 2% by weight of binder was tested

BBR properties of similar PG grades modified with different additives were similar, but the direct tension results of the polymer-modified binders were higher than for other additives.



DIRECT TENSION STRENGTH RESULTS, MPa

TEMP	64-34C	64-34 ELVALOY + PPA	64-34 1101	64-34 1184	
-21	3.22				
-24	3.9	5.06	5.06	4.64	
-27		5.52	5.35	4.31	

INFORMATION AVAILABLE

5. Orange G., Dupuis D., Martin J.V., Farcas F., Such C., Marcante B., "Chemical Modification of Bitumen through Polyphosphoric Acid: Properties-Microstructure Relationship", *3rd Eurasphalt Eurobitume Congress* (Vienna 05/04), Book I p733-745.

Examined the effect of PPA and PPA + SBS polymer additives on binder properties.

Mechanisms by which PPA interacts with asphalt were proposed based on P^{31} NMR

Moisture sensitivity tests conducted on aggregates combined with PPA modified binders were discussed and good adhesion was found.



INFORMATION AVAILABLE

6. Ajideh, H., Rangel, A., Bahia, H., “Can Chemical Modification of Paving Asphalt be Equated to Polymer Modification: a Laboratory Study”, Transportation Research Board 2004, CD-ROM of papers presented.

Comparisons between a control, 2 binders modified with 2% phosphoric acid, and a PMA were made.

Binder tests indicated

- ✓ Rutting resistance improvement for both acid modified and PMA materials.
- ✓ Acid modified had higher viscosity PMA had greater elasticity.
- ✓ Thin film aging of acid modified appeared greater than for PMA.
- ✓ Fatigue results of acid modified significantly improved over the control.
- ✓ TSR results for PMA were better than for acid modified. No TSR data for the control was presented



INFORMATION AVAILABLE

Rocky Mountain Asphalt User Producer Group (RMAUPG) meeting in March of 2003 a day devoted to discussions about PPA modified binders and mixes. Presenters were

Dave Jones—Owens Corning/Trumbul

Gerald Reinke—Mathy Construction/MTE

Gaylon Baumgardner—Ergon Refining/Paragon

Bob McGennis—Koch Southwest, now ??

Bruno Marcant & John Hanrahan—Rhodia now Innophos

Laird Weishan—Nebraska DOR

These presentations are available through the Rocky Mt Asphalt User Producer Group.



INFORMATION AVAILABLE

WESTERN RESEARCH INSTITUTE 2004 SYMPOSIUM ON ASPHALT ADDITIVES

Mike Falkiewicz & Ken Grzybowski—Astaris & PRI

Gaylon Baumgardner—Ergon Refining/Paragon

These presentations can be downloaded from WRI website



WHAT IS BEING DONE

1. FHWA IS UNDERTAKING AN INVESTIGATION OF THE IMPACT OF ACID MODIFICATION ON THE PROPERTIES OF BINDERS AND THE PERFORMANCE OF MIXES
 - OBTAIN A COPY OF TERRY ARNOLD'S SEPT. 2004 ETG PRESENTATION FOR THE INITIAL WORK PLAN
2. THE ASPHALT INSTITUTE IS WORKING ON AN "INFORMATION SERIES" IS-XXX DOCUMENT THAT WILL ATTEMPT TO PULL TOGETHER THE CURRENTLY AVAILABLE INFORMATION ON THE SUBJECT.
 - TASK GROUP HEADED BY MARK BUNCHER & COMPRISED OF INDUSTRY REPRESENTATIVES WHO ARE MEMBERS OF THE ASPHALT INSTITUTE. PRO'S & CON'S CONSIDERED



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PG 58-34 ACID MODIFIED
4.5 MILES, PAVED JULY 2002

FEB 26 2004

**PG 58-34 ACID
MODIFIED,
SUMMER 2002**

JAN 29 2005

**HOUSTON CTY,
MN CTH 16 @ La
CRESCENT**

**PG 58-34 ACID
MODIFIED,
SUMMER 2002**



JAN 29 2005

**HOUSTON CTY,
MN CTH 13 @
HOUSTON, MN**

**PG 58-34 ACID
MODIFIED,
SUMMER 2002**



JAN 29 2005

PG 64-28
POLYMER + PPA
SUMMER 2002



JAN 29 2005

October 2003



US 60 @ Thomas Rd (no AR-ACFC yet)
MCGENNIS, RMAUPG 2004



US 60, Clovis, PSI = 4.45

PG 70-22, 2001

MCGENNIS, RMAUPG 2004

CONCLUSIONS

ACID MODIFICATION γ_p POLYMER
MODIFICATION

DON'T CONFUSE PPA ONLY MODIFICATION WITH
POLYMER + PPA MODIFICATION

ACID MODIFIED BINDERS DON'T SEEM TO AGE
MORE EXTENSIVELY THAN ORIGINAL BINDER

BINDER EXTRACTED FROM POLYMER ONLY AND
POLYMER + PPA MIXES EXHIBITED SIMILAR
HIGH TEMPERATURE AND LOW
TEMPERATURE PROPERTIES & AGING RATES

THE ISSUE OF FATIGUE

1. OUR DATA INDICATES THAT FATIGUE OF MIXES USING POLYMER IS BETTER THAN THAT OF MIXES WITH ACID ONLY—UP TO A POINT
 1. ONCE THE MIX HAS BEEN AGED THE MIX FATIGUE RESULTS SEEM TO MERGE.
 2. BAHIA, ET. AL PRESENTED RESULTS AT 2004 TRB SHOWING COMPARABLE FATIGUE PROPERTIES FOR ACID AND POLYMER MODIFIED PAV RESIDUES

THE ISSUE OF MOISTURE SENSITIVITY

1. THIS IS A MIX PROBLEM AND SHOULD BE TREATED AS A MIX PROBLEM
 - A. BINDER COMPATIBILITY
 - B. AGGREGATE, BINDER, PPA INTERACTIONS
2. THERE ARE COMPATIBLE ANTI-STRIPPING ADDITIVES AVAILABLE—USE THEM WHEN NEEDED
 1. FOR MANY AGGREGATES THE PPA APPEARS TO SERVE AS AN ANTI-STRIP
3. THE TOOLS ARE AVAILABLE TO PREVENT INCOMPATIBLE SYSTEMS FROM REACHING THE ROAD—USE THEM

A FINAL COMMENT

**ABOVE ALL ELSE COMMUNICATION
BETWEEN AGENCY, SUPPLIER AND
CONTRACTOR IS ESSENTIAL TO SUCCESS**



"OF COURSE YOU CAN'T REPLICATE MY EXPERIMENT.
THERE'S A SECRET INCANTATION THAT YOU HAVE TO CHANT,
AND I'M NOT TELLING IT TO ANYONE."