DOUBLE CLICK ON THE SMALL YELLOW DIALOG BUBBLE TO SEE NOTES.
OR JUST PUT MOUSE CURSOR ON THE DIALOG BUBBLE TO READ THE NOTE.

THE FOLLOWING GROUP OF SLIDES WAS PRESENTED AT THE ROCKY MOUNTAIN ASPHALT USER PRODUCER GROUP MEETING ON MARCH 3, 2004. SLIDES WHICH HAVE A RED  IN THE UPPER LEFT HAND CORNER HAVE NOTES WRITTEN FOR THEM TO DISCUSS THE DATA PRESENTED. YOU SHOULD READ THESE NOTES FOR THE DETAILS BEHIND THE DATA

ON MARCH 3, 2004 SIX INDIVIDUALS PRESENTED DISCUSSIONS ON THE USE AND IMPACT OF ACID MODIFICATION IN ASPHALT AT THE ROCKY MOUNTAIN ASPHALT USER PRODUCER GROUP MEETING.

IN ORDER OF PRESENTATION THE WERE

DAVE JONES-TRUMBULL ASPHALT

GERALD REINKE-MTE SERVICES, INC.

GAYLON BAUMGARTNER- PARAGON TECHNICAL SERVICES

BRUNO MARCANT-RHODIA

LAIRD WEISHAN- NEBRASKA DEPT OF ROADS

BOB MCGENNIS-KOCH PAVEMENT SOLUTIONS

MOISTURE SENSITIVITY OF ACID MODIFIED ASPHALT & MIXTURES WITH and WITHOUT ANTI-STRIPPING AGENTS

FOR PRESENTATION AT THE ROCKY MOUNTAIN ASPHALT USER PRODUCER GROUP MEETING

By Gerald Reinke—MTE Services, Inc.

MARCH 3, 2004 SANTE FE, NM

OR

"It's not what we don't know that hurts, it's what we know that ain't so" – Will Rogers

OR

"Quod enim mavult homo verum esse, id poitus credit"

What man wishes were true, he more readily believes.

SOME BACKGROUND INFORMATION

1. DESPITE RECENT FLURRY OF CONCERNS RELATED TO ACID MODIFICATION OF ASPHALT THE INCORPORATION OF ACIDIC CHEMICALS INTO ASPHALTIC PRODUCTS & BITUMINOUS PAVING MATERIALS HAS BEEN THE SUBJECT OF RESEARCH FOR MANY YEARS.
   - PATENT REFERENCE FROM 1939 (BURK 2179208) STANDARD OIL, DIRECTED TOWARDS MANUFACTURING ASPHALT WITH THE USE OF ACIDS AND REDUCED TIMES OF AIR BLOWING
   - ALEXANDER IN 1973 (3751278), TOSCO-LION REFINING CO., DIRECTED TOWARDS THE USE OF PHOSPHORIC ACIDS TO PRODUCE PAVING GRADE ASPHALT WITHOUT BLOWING

BACKGROUND CONTINUED

- McGINNIS (ED) 1991 (CHEVRON) USE OF SOLVENT EXTRACTED ASPHALT, A BITUMINOUS MATERIAL AND PHOSPHORIC ACID
- MORAN (ESSO) 1989, 1991, 1992 USE OF ACID AND A WIDE RANGE OF POLYMERS
- REINKE, ENGBER (MTE) 2001, 2003 USE OF ACID WITH EPOXY GROUP BEARING TERPOLYMERS
- BAUMGARTNER, ET. AL (ERGON) 2000, 2001 METHODS OF PREPARING POLYPHOSPHORIC ACID AND POLYMER ASPHALT BLENDS
- PUZIC, ET. AL (EXXON RESEARCH) 1996, 1997 USE OF ACID AND DIENE CONTAINING POLYMERS

BACKGROUND CONTINUED

- VAN DER WERFF, ET. AL (SHELL OIL) 1996 USE OF ACID AND GLYCIDYL CONTAINING POLYMERS. (MAINLY DIRECTED TOWARDS ROOFING APPLICATIONS)
- GERMANAUD ET. AL (ELF FRANCE) 1997 USE OF SBS, SULFUR AND ACID TO PRODUCE PMA
- PLANCHE, ET. AL (ELF FRANCE) 2000 USE OF EPOXY BEARING POLYMERS, ACID IN CONJUNCTION WITH SBS

I KNOW WHAT YOU'RE THINKING

JUST BECAUSE INDIVIDUALS AND COMPANIES ENGAGE IN OBTAINING PATENTS ON A PARTICULAR TECHNOLOGY DOESN'T NECESSARILY MEAN THAT IT IS WORTHWHILE!

THERE ARE REALLY 2 AND PERHAPS 3 ISSUES 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
3. THE USE OF AN ACID CATALYST AS PART OF THE OXIDIZING PROCESS TO PRODUCE A PG GRADED BINDER.

BUT LET'S NOT FORGET OL' WILL ROGERS

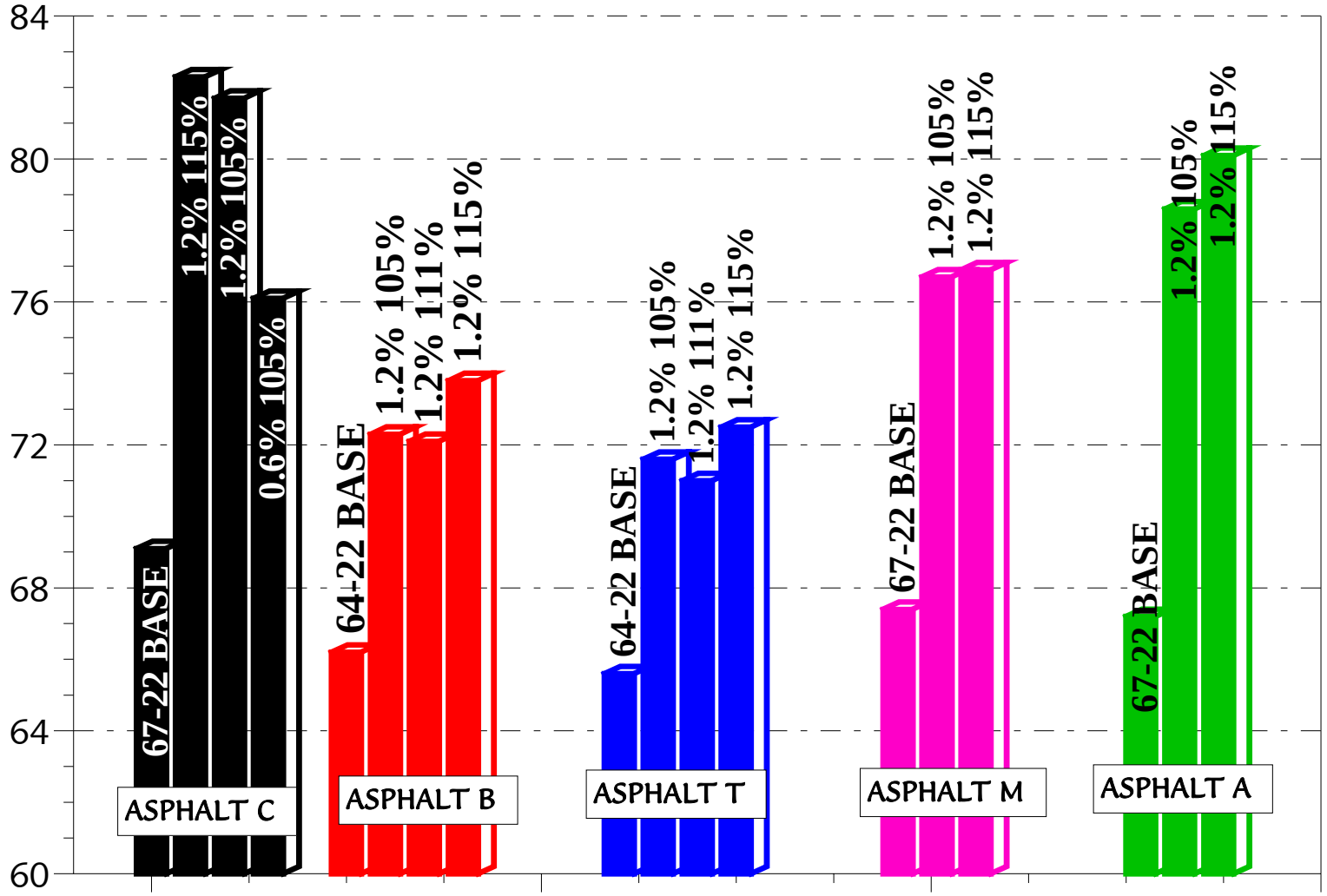
WHAT IS IT THAT WE KNOW AND WHAT IS IT THAT WE KNOW THAT AIN'T SO

WE *KNOW*? THAT BITUMINOUS MIXES MADE WITH ACID IN THE ASPHALT

1. **AGE FASTER (THAN ?)**
2. **ARE MORE SUSCEPTIBLE TO THERMAL CRACKING**
3. **ARE MORE SUSCEPTIBLE TO FATIGUE FAILURE**
4. **ARE MORE SUSCEPTIBLE TO MOISTURE (THAN ?)**
5. **CAN'T BE BLENDED WITH ANTI-STRIPS**
6. **WILL REACT DETRIMENTALLY WITH CERTAIN TYPES OF AGGREGATES**

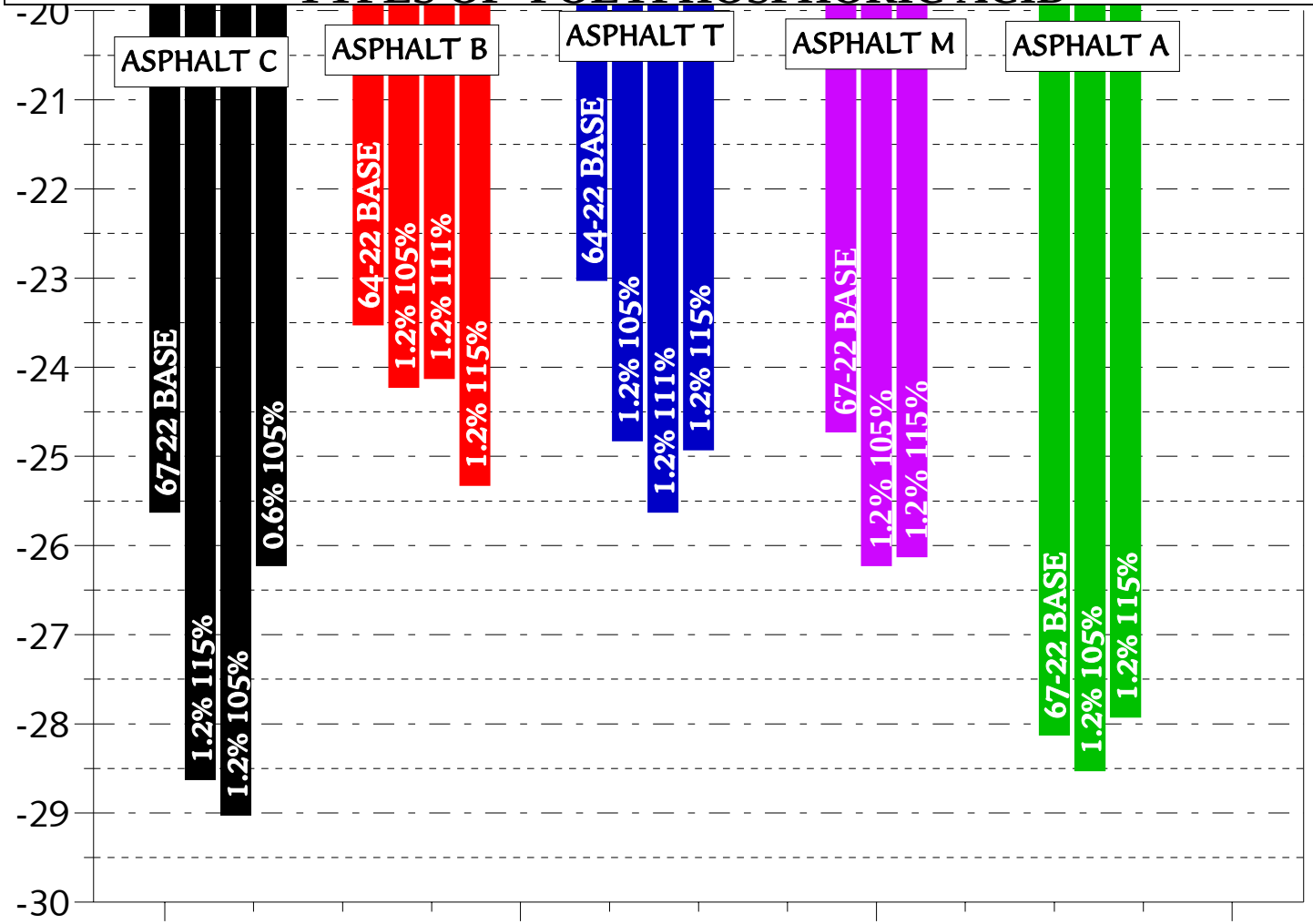
IMPACT OF THE ADDITION OF ACID ON THE PROPERTIES OF ASPHALT BINDERS AND MIXES

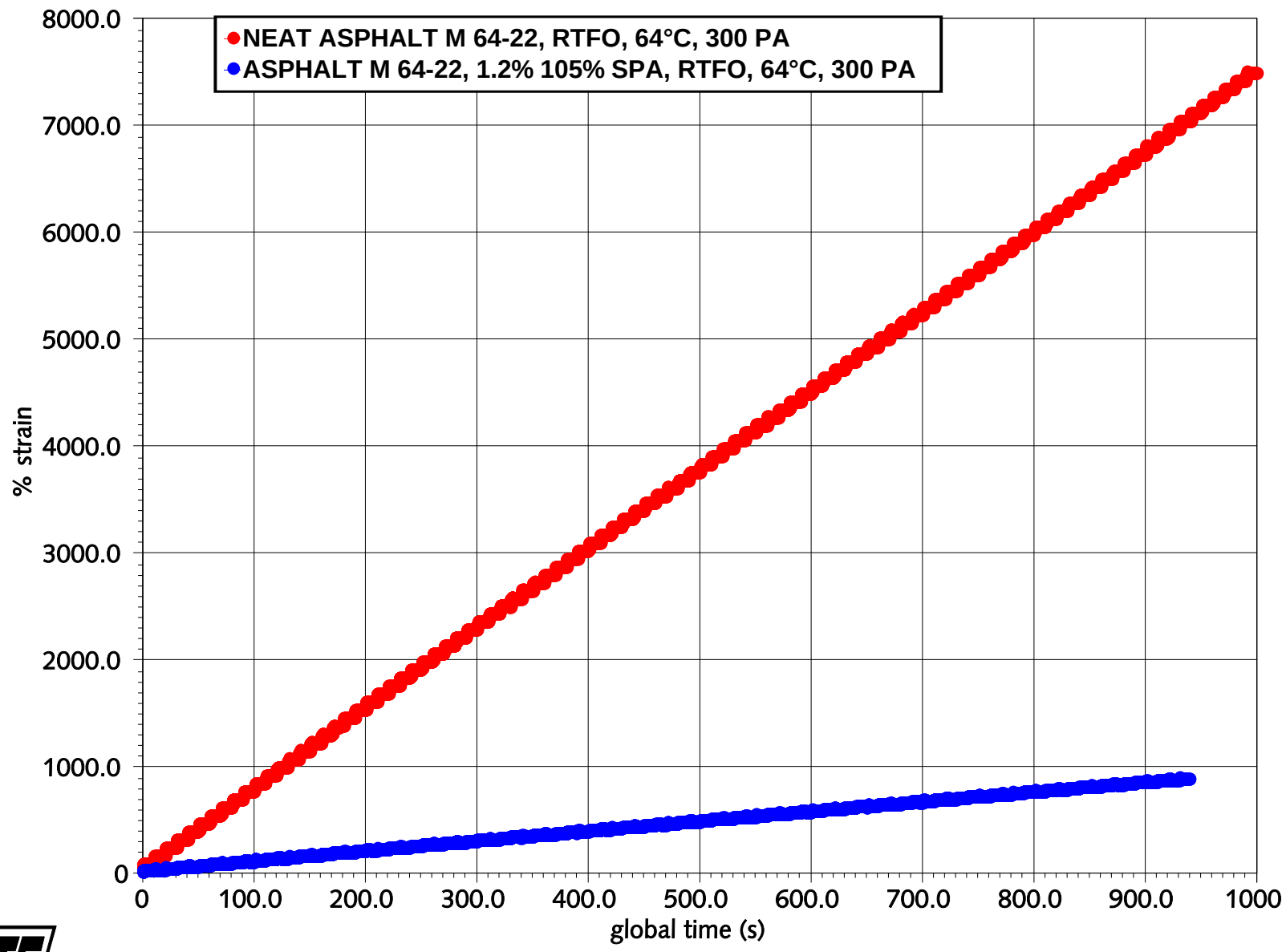
IMPACT ON HIGH TEMPERATURE PG GRADE ADDITION OF 1.2% OF DIFFERENT TYPES OF POLYPHOSPHORIC ACID

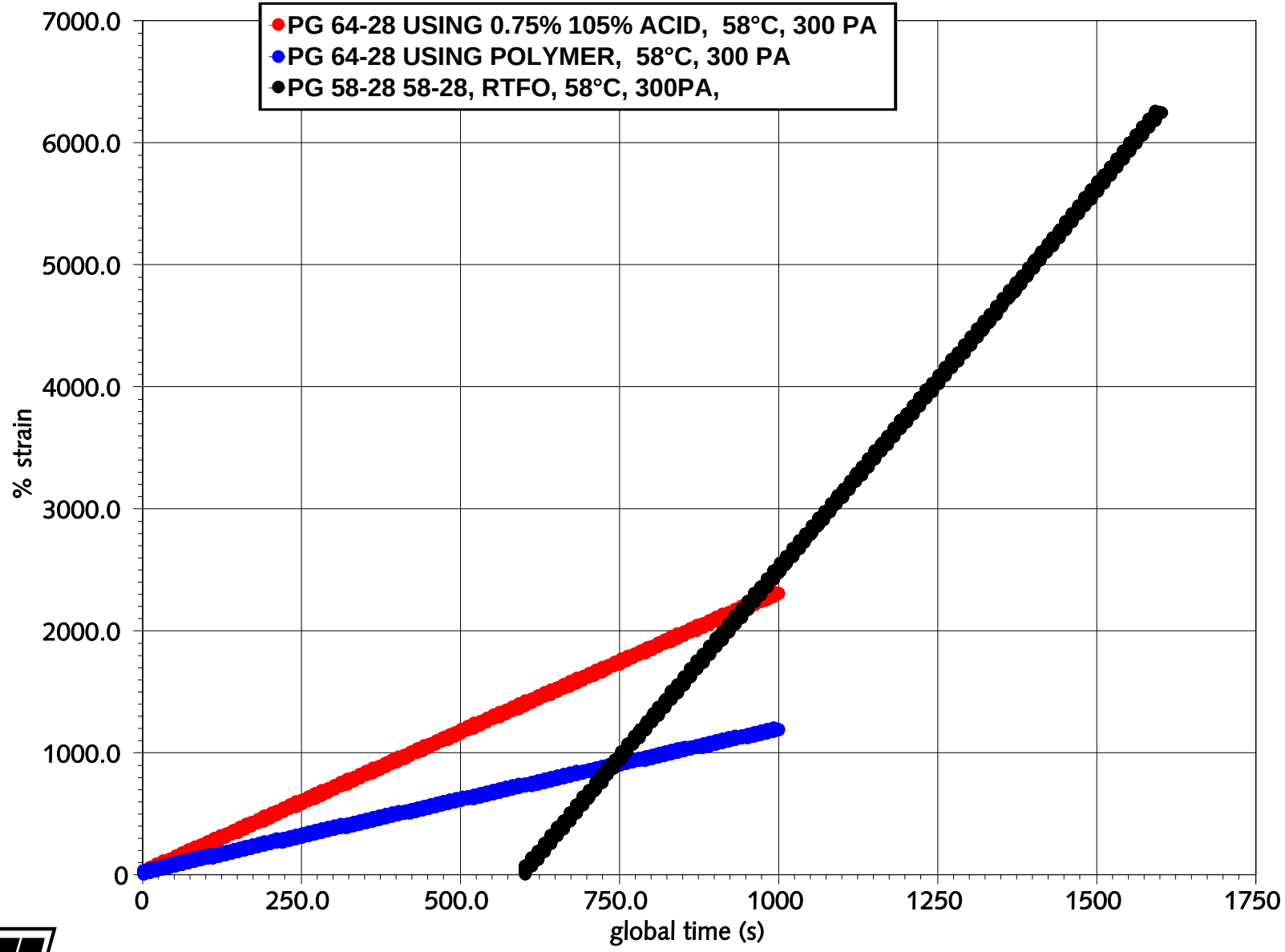


IMPACT ON CRITICAL CRACKING TEMPERATURE OF BINDER

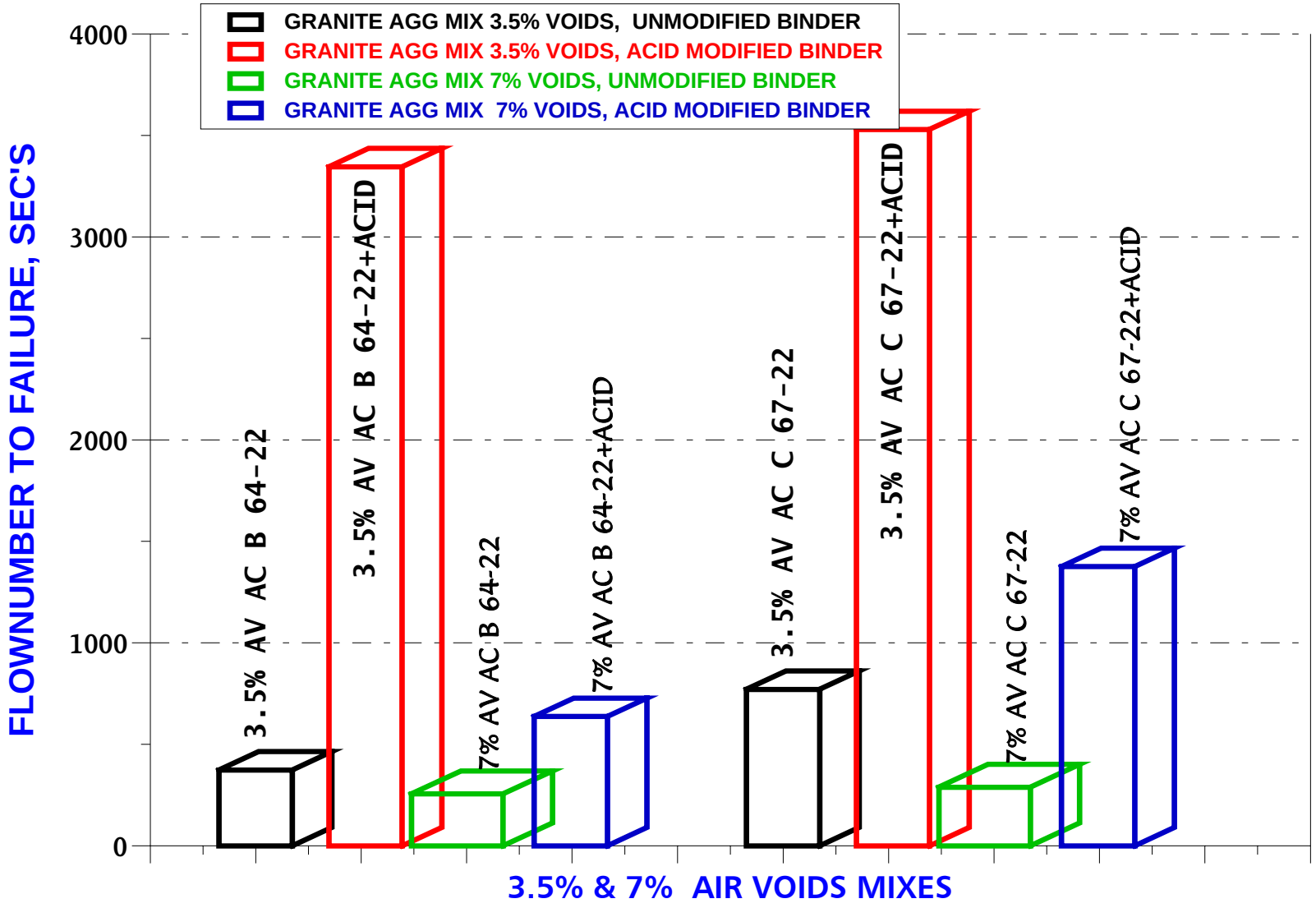
ADDITION OF 1.2% (0.6% FOR ONE SAMPLE OF DIFFERENT TYPES OF POLYPHOSPHORIC ACID



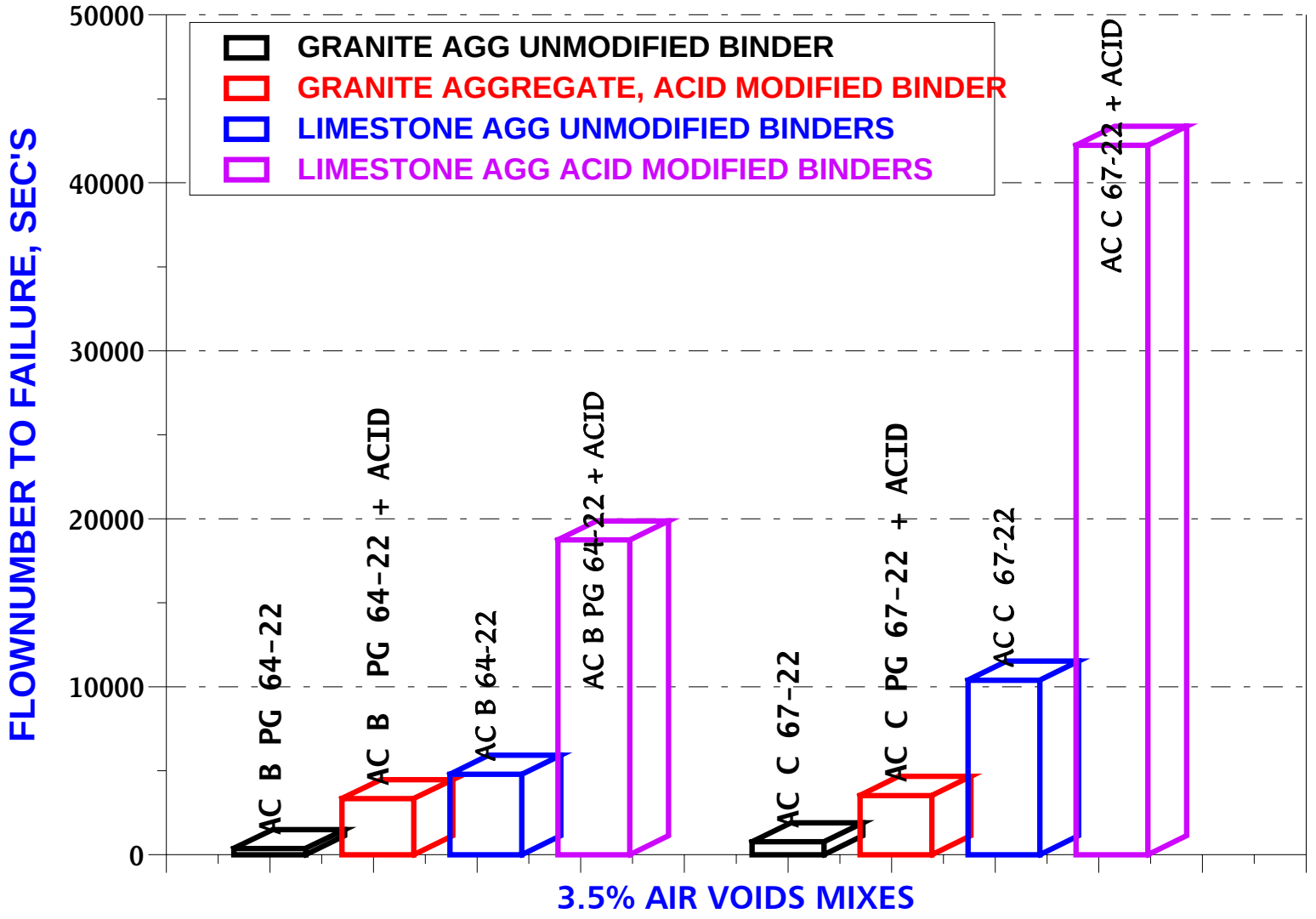

ASPHALT M 64-22, RTFO, 64°C, 300 PA CUM CRT-0001c
NEAT ASPHALT M 64-22, RTFO, 64°C, 300 PA
ASPHALT M 64-22, 1.2% 105% SPA, RTFO, 64°C, 300 PA
% strain
8000.0
7000.0
6000.0
5000.0
4000.0
3000.0
2000.0
1000.0
0
0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
900.0
1000
global time (s)


PG 58-28 & PG 64-28 MADE FROM IT, 58°C, 300 PACUM CRT-0001c
PG 64-28 USING 0.75% 105% ACID, 58°C, 300 PA
PG 64-28 USING POLYMER, 58°C, 300 PA
PG 58-28 58-28, RTFO, 58°C, 300PA,
% strain
global time (s)
0
1000.0
2000.0
3000.0
4000.0
5000.0
6000.0
7000.0
0
250.0
500.0
750.0
1000
1250
1500
1750

FLOWNUMBER FROM REPEATED CREEP & RECVOERY TEST
3.5% & 7% AIR VOIDS GRANITE MIXES: 68 KPA STRESS, 58° C TEST TEMP
FLOWNUMBER= TIME TO TERTIARY FLOW

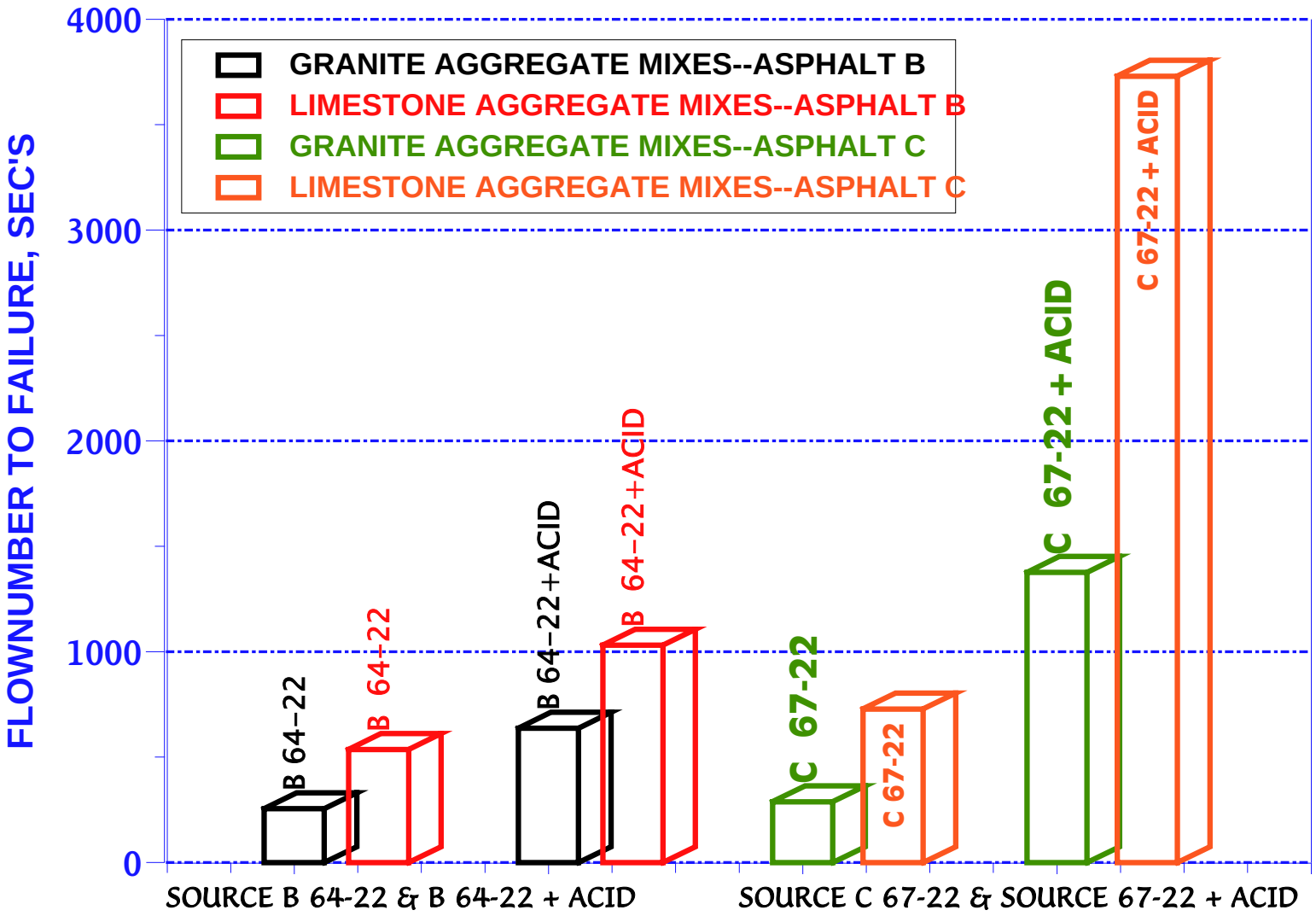


FLOWNUMBER FROM REPEATED CREEP & RECVOERY TEST
68 KPA STRESS, 58° C TEST TEMP
FLOWNUMBER= TIME TO TERTIARY FLOW

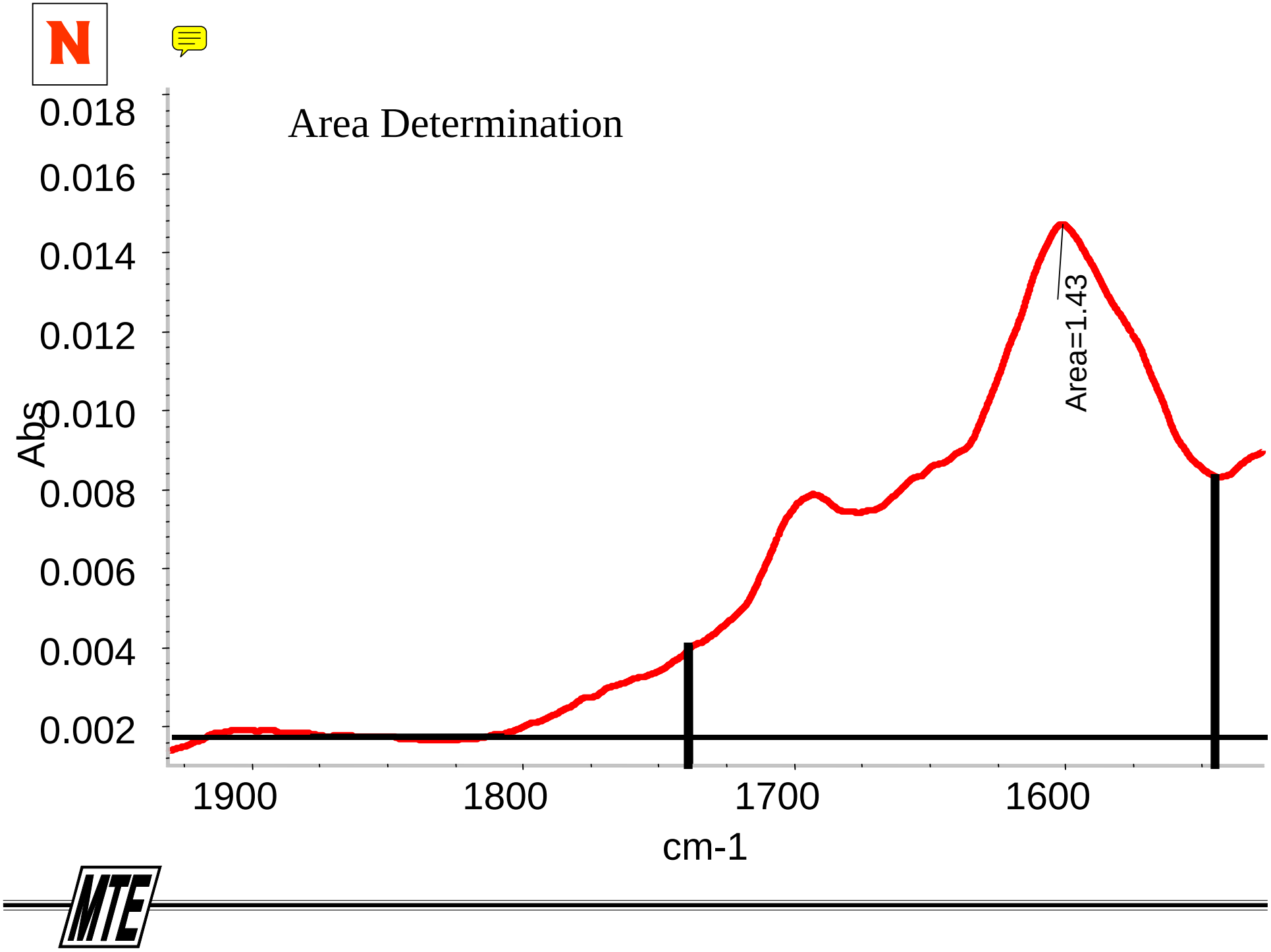


N

FLOWNUMBER TO FAILURE FOR ASPHALTS B AND C WITH AND WITHOUT ACID AT 7% AIR VOIDS, 68 KPA STRESS, 58° C TEST TEMP FOR GRANITE & LIMESTONE AGGREGATES

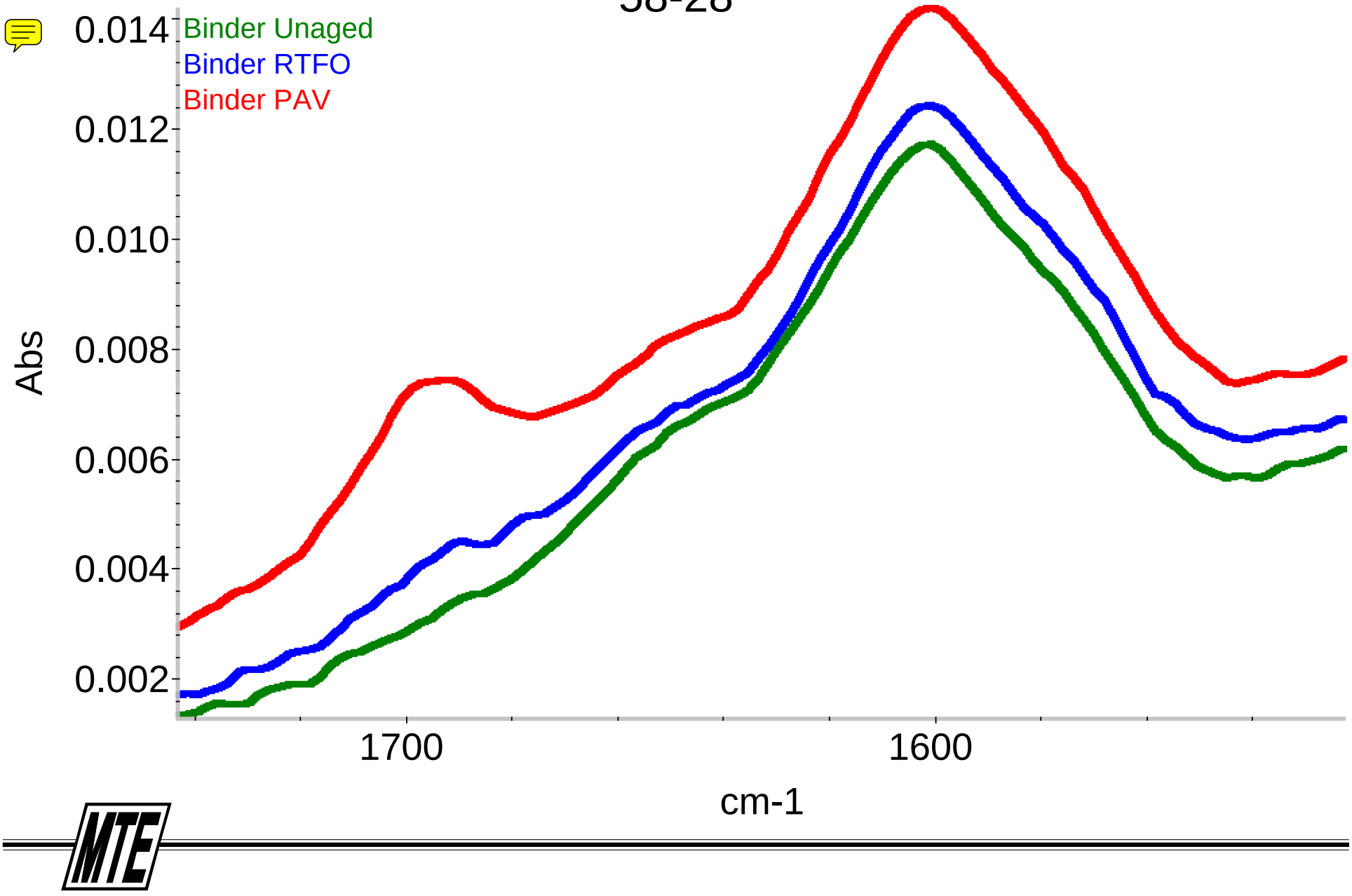


IMPACT OF AGING ON PROPERTIES OF MIXES PRODUCED WITH ACID CONTAINING BINDERS


Area Determination
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
Abs
Area=1.43
1900
1800
1700
1600
cm-1

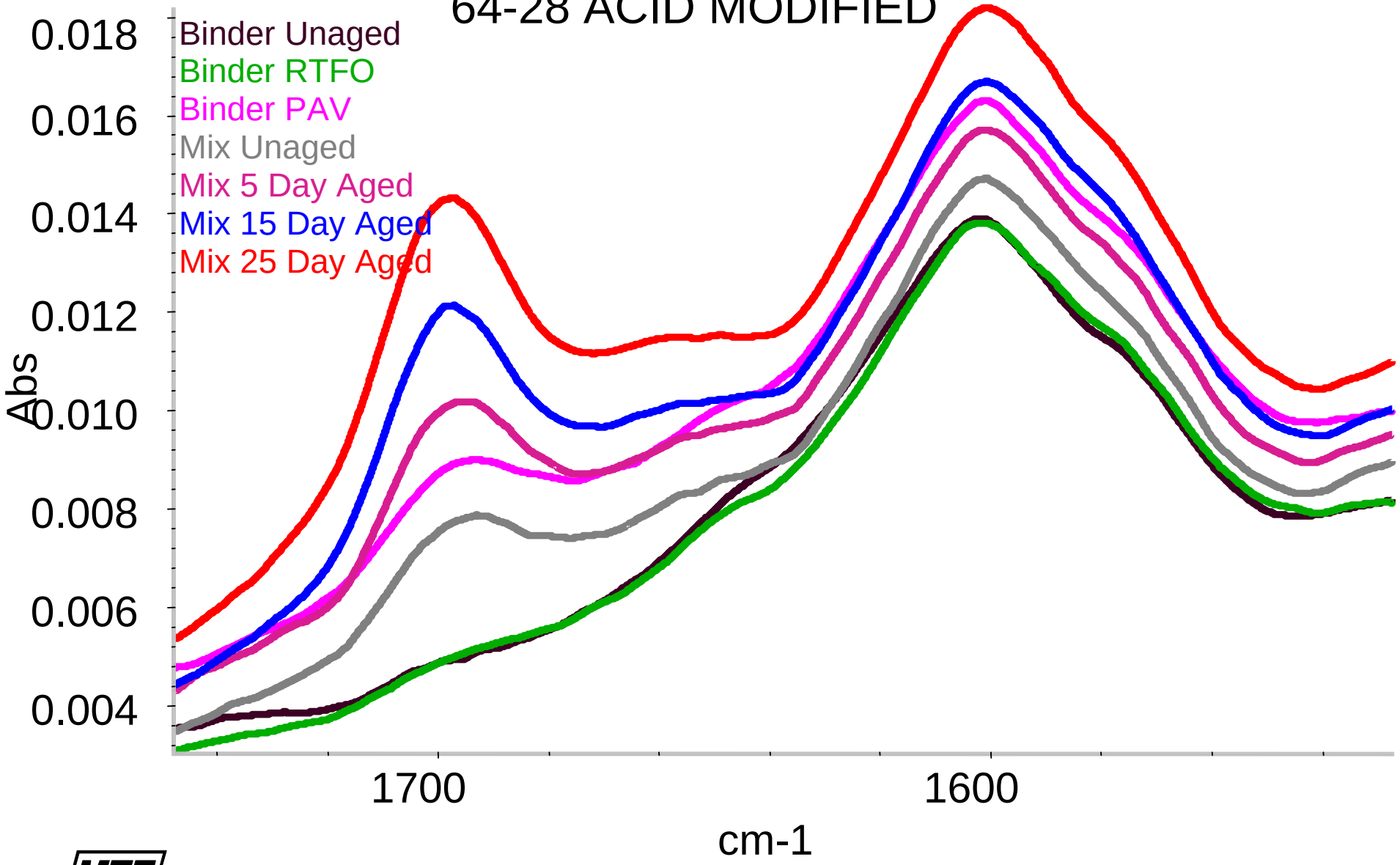
Aging Study

58-28



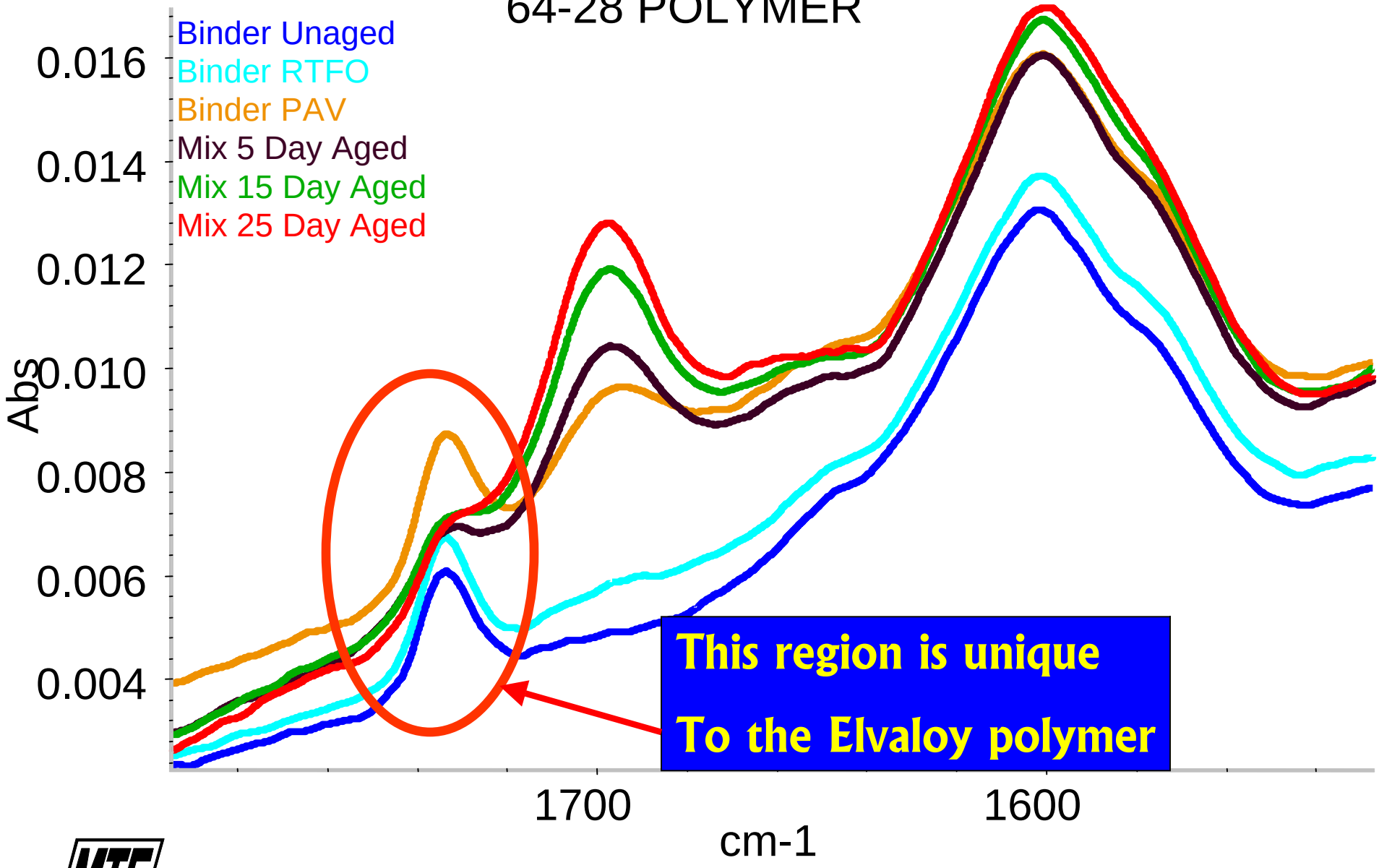
Aging Study

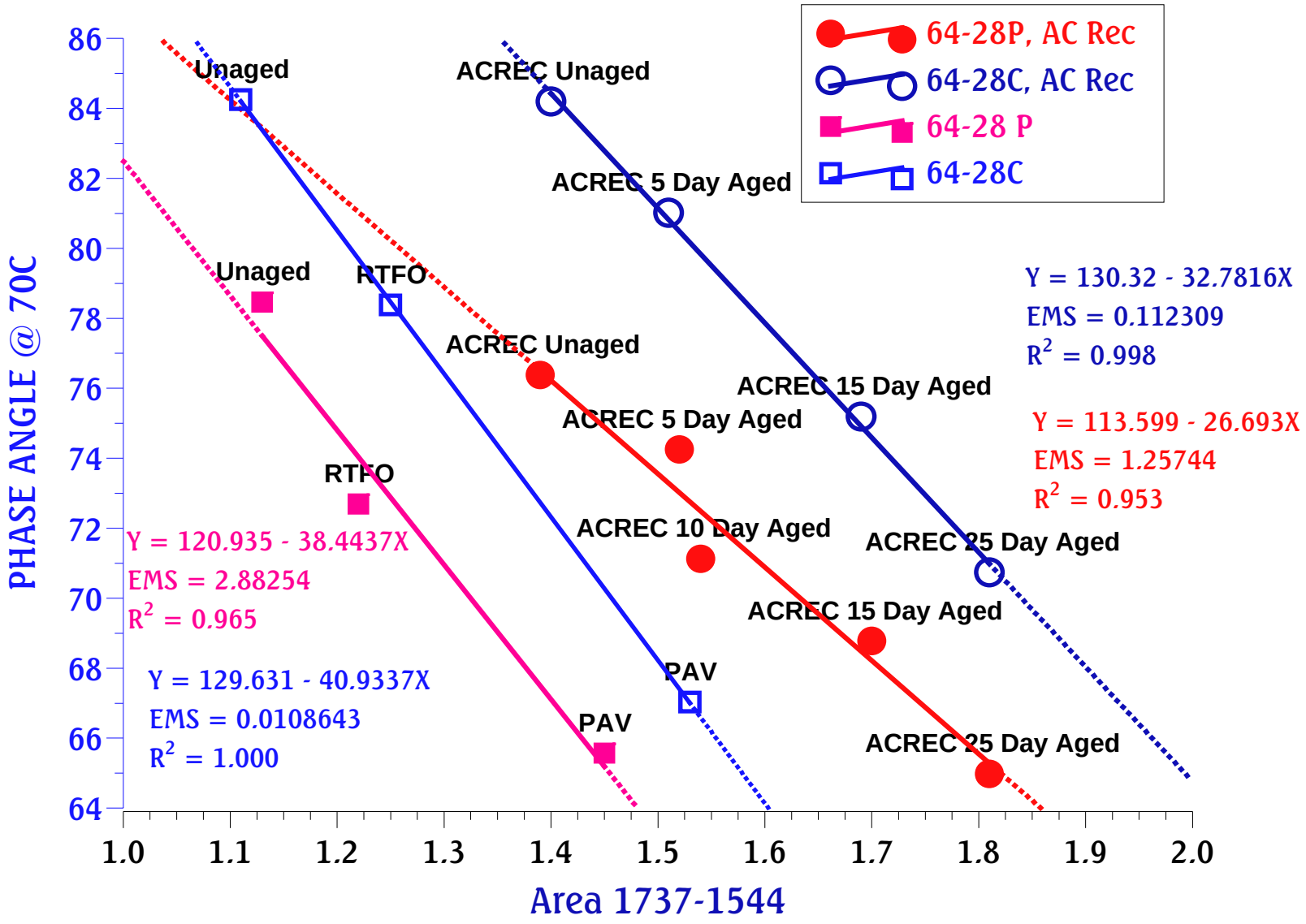
64-28 ACID MODIFIED

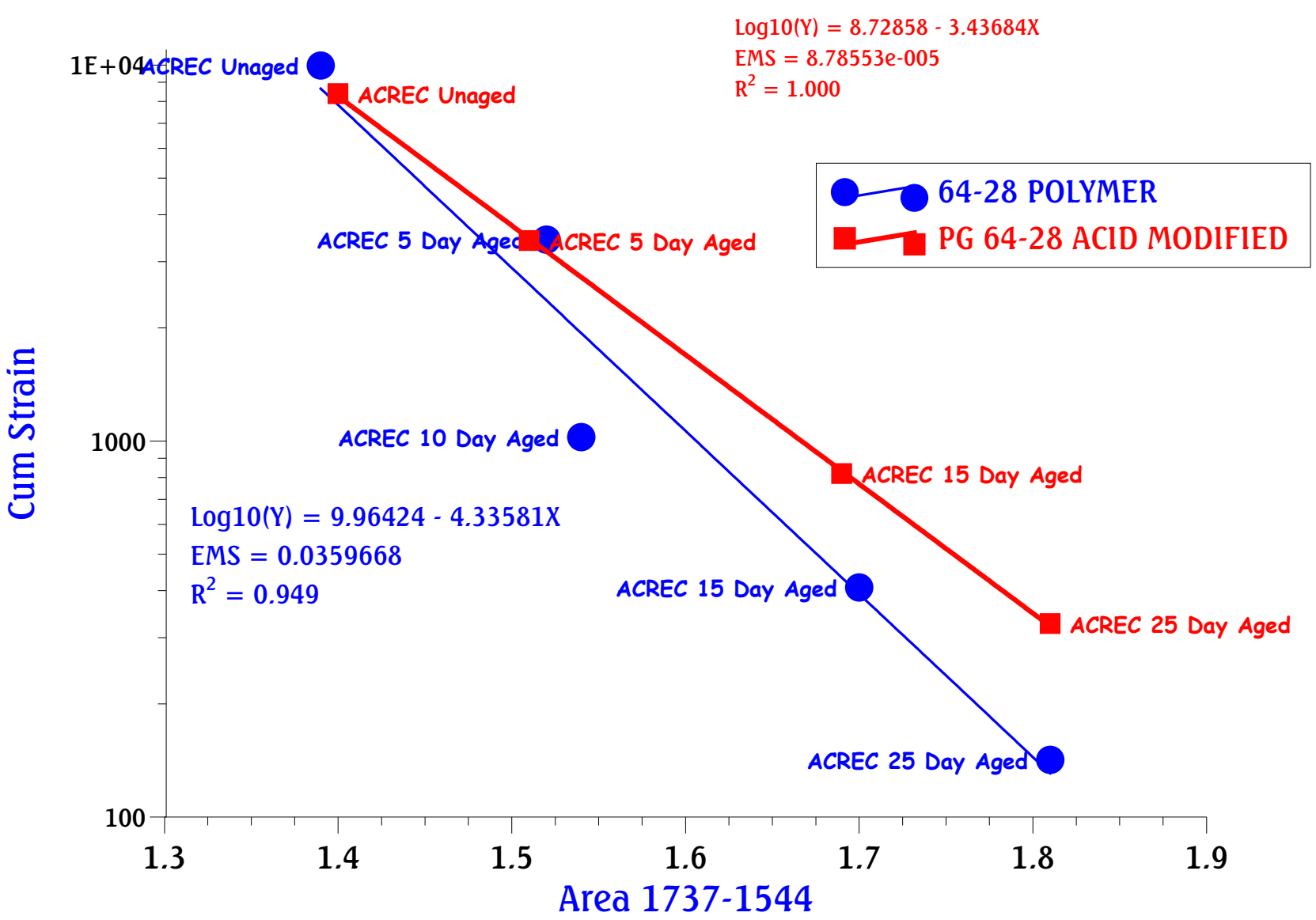


Aging Study

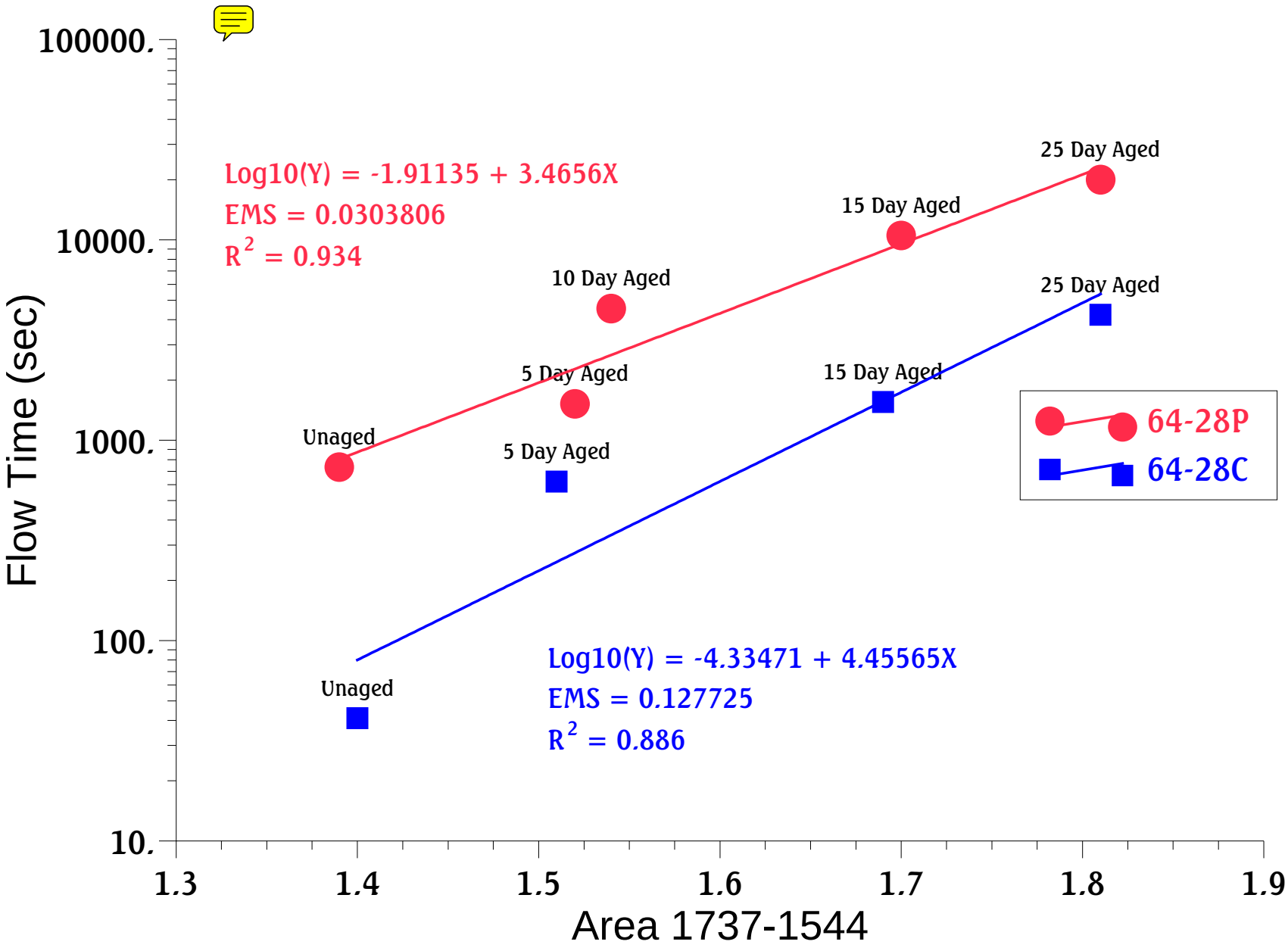
64-28 POLYMER



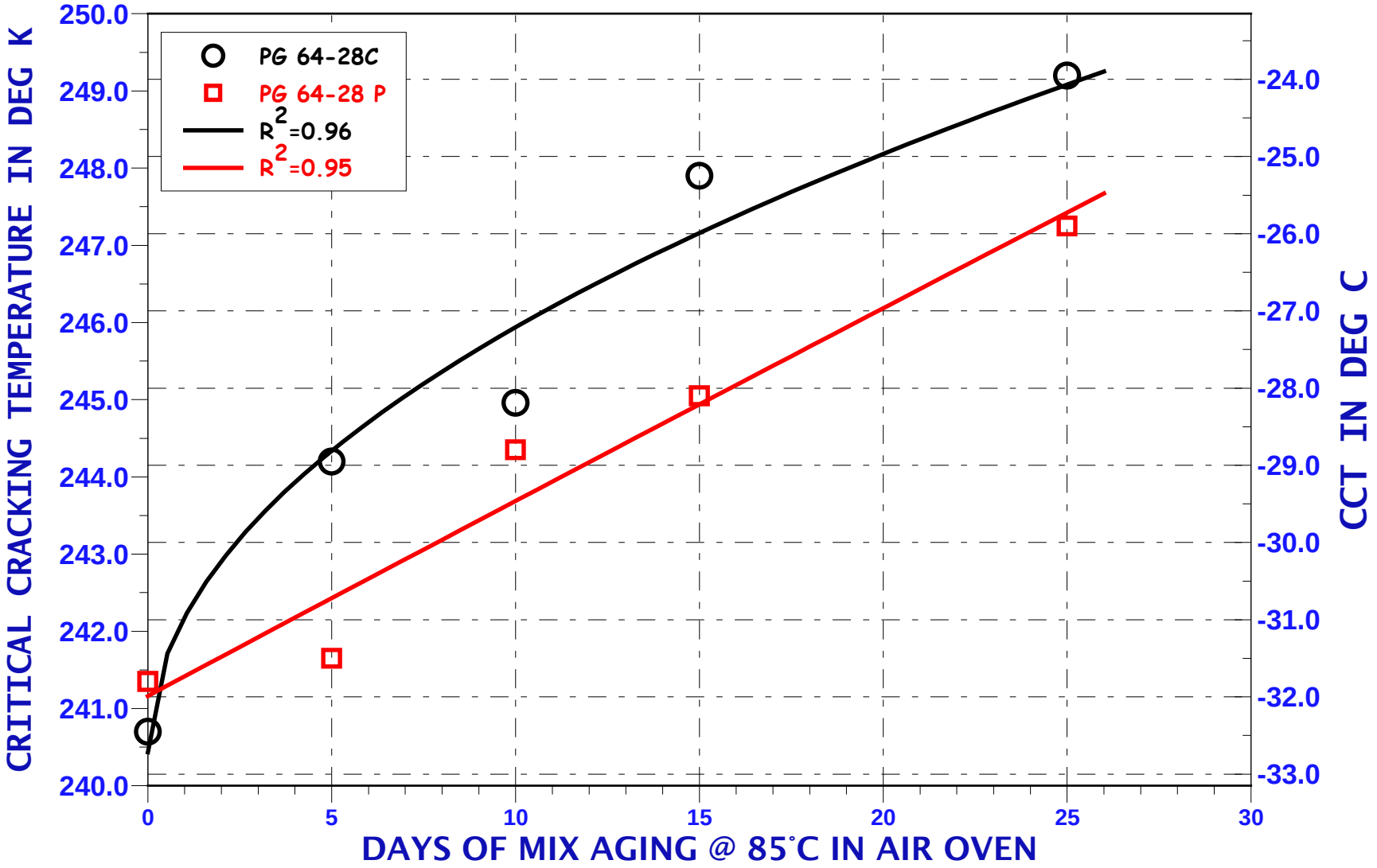

64-28P, AC Rec
64-28C, AC Rec
64-28 P
64-28C
Unaged
ACREC Unaged
ACREC 5 Day Aged
Unaged
RTFO
ACREC Unaged
ACREC 15 Day Aged
ACREC 5 Day Aged
RTFO
ACREC 10 Day Aged
ACREC 25 Day Aged
ACREC 15 Day Aged
PAV
PAV
ACREC 25 Day Aged
Y = 130.32 - 32.7816X
EMS = 0.112309
R2 = 0.998
Y = 113.599 - 26.693X
EMS = 1.25744
R2 = 0.953
Y = 120.935 - 38.4437X
EMS = 2.88254
R2 = 0.965
Y = 129.631 - 40.9337X
EMS = 0.0108643
R2 = 1.000
PHASE ANGLE @ 70C
86
84
82
80
78
76
74
72
70
68
66
64
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
Area 1737-1544



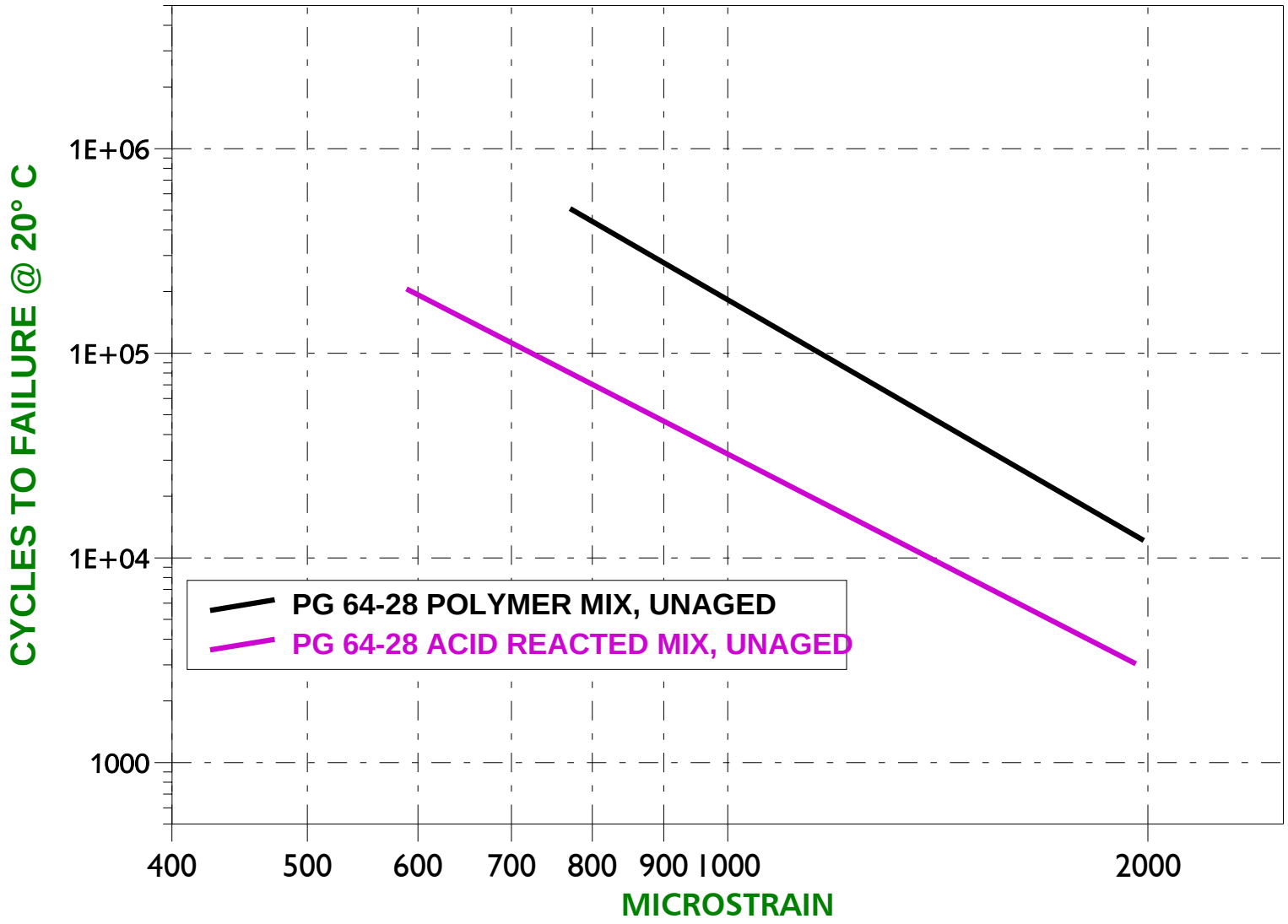
12/08/02 09:35:26 E:\IR Data\Mathy Spectra\Aging Study\Area 1737-1544 vs Cum Strain.spf


100000.
10000.
1000.
100.
10.
Flow Time (sec)
Log10(Y) = -1.91135 + 3.4656X
EMS = 0.0303806
R2 = 0.934
25 Day Aged
15 Day Aged
10 Day Aged
5 Day Aged
Unaged
25 Day Aged
15 Day Aged
5 Day Aged
Unaged
Log10(Y) = -4.33471 + 4.45565X
EMS = 0.127725
R2 = 0.886
64-28P
64-28C
1.3
1.4
1.5
1.6
1.7
1.8
1.9
Area 1737-1544

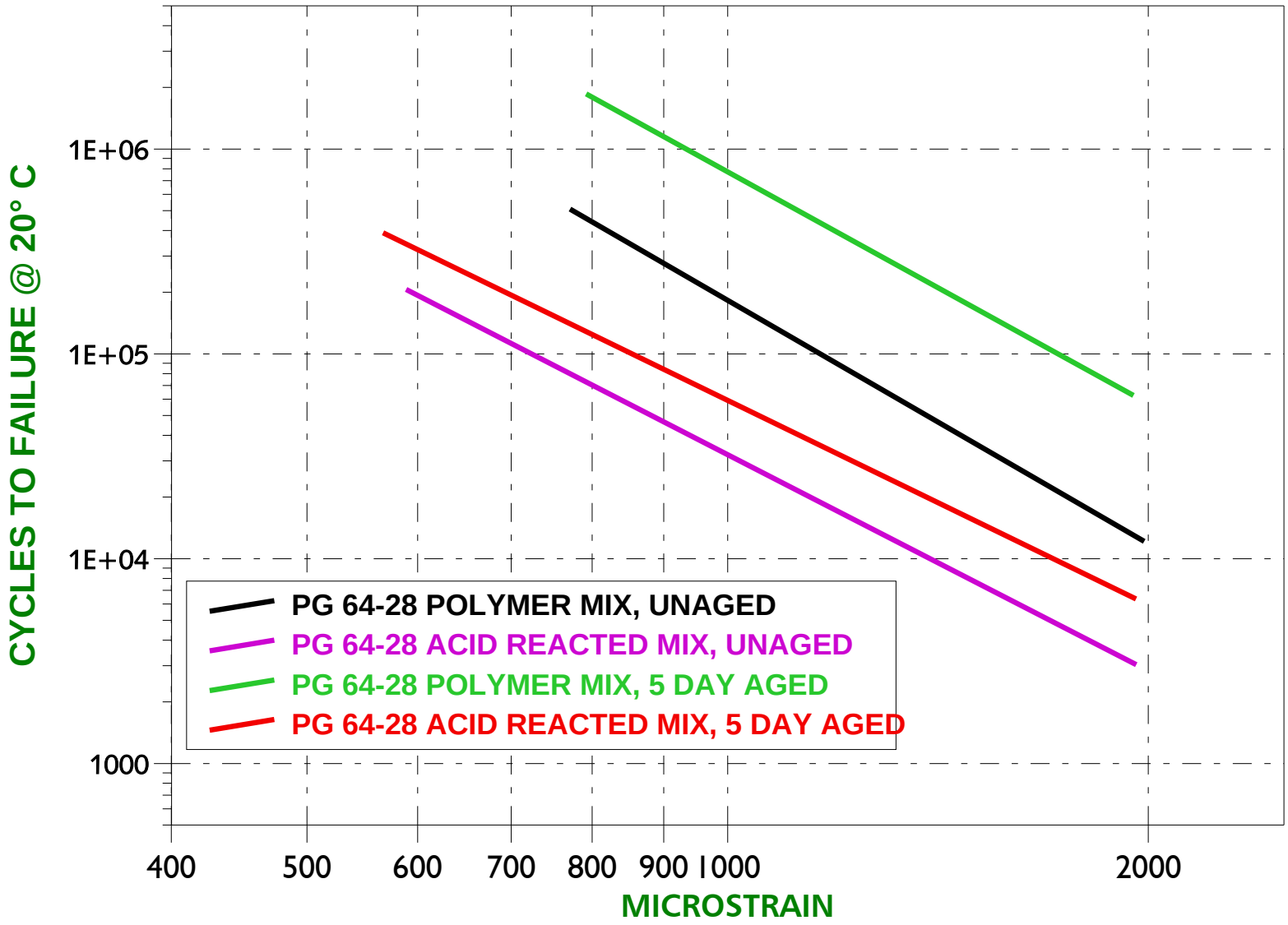
CRITICAL CRACKING TEMPERATURE OF BINDER RECOVERED FROM AGED MIXES FOR PG 64-28P & PG 64-28 C



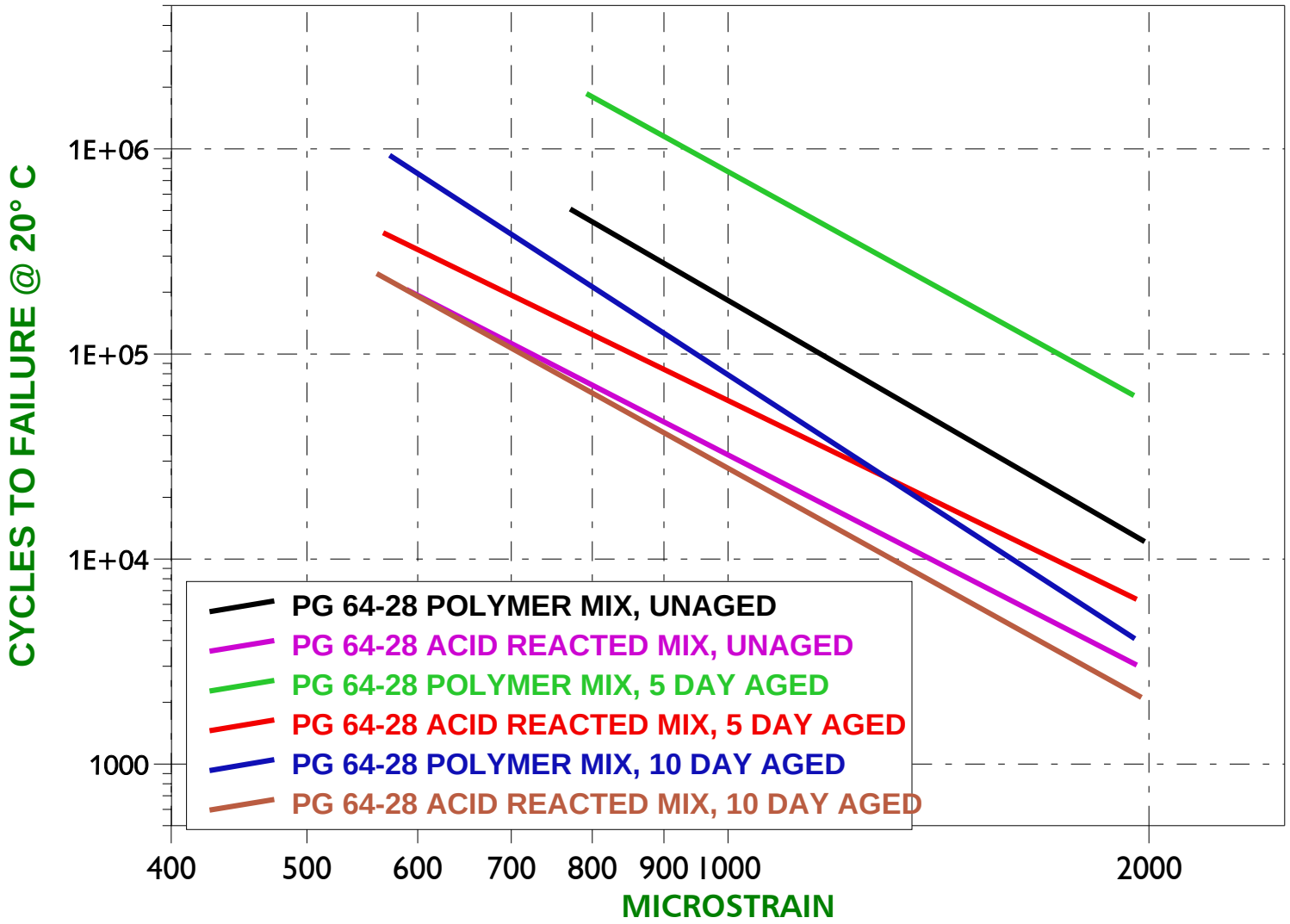
COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED



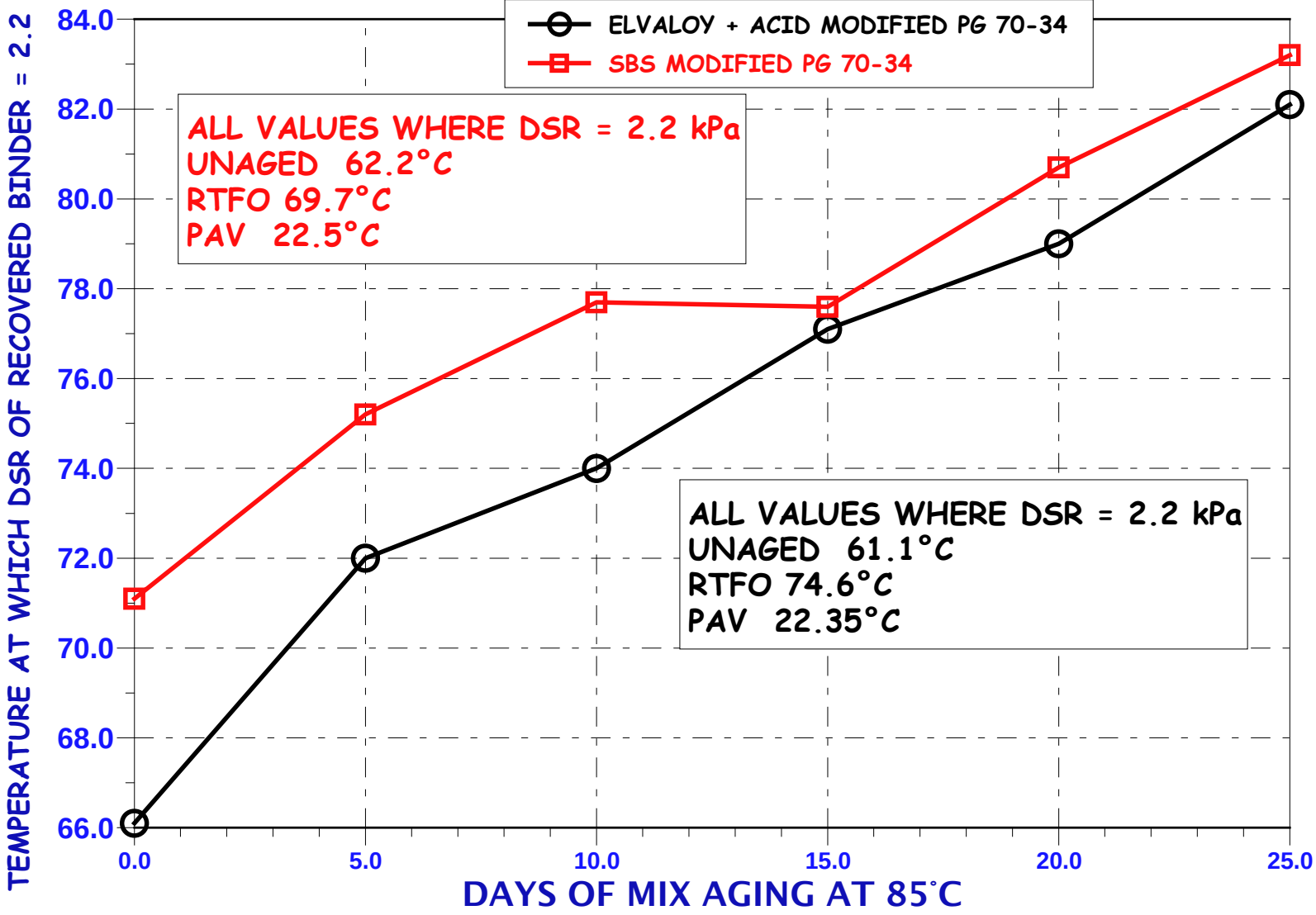
COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED

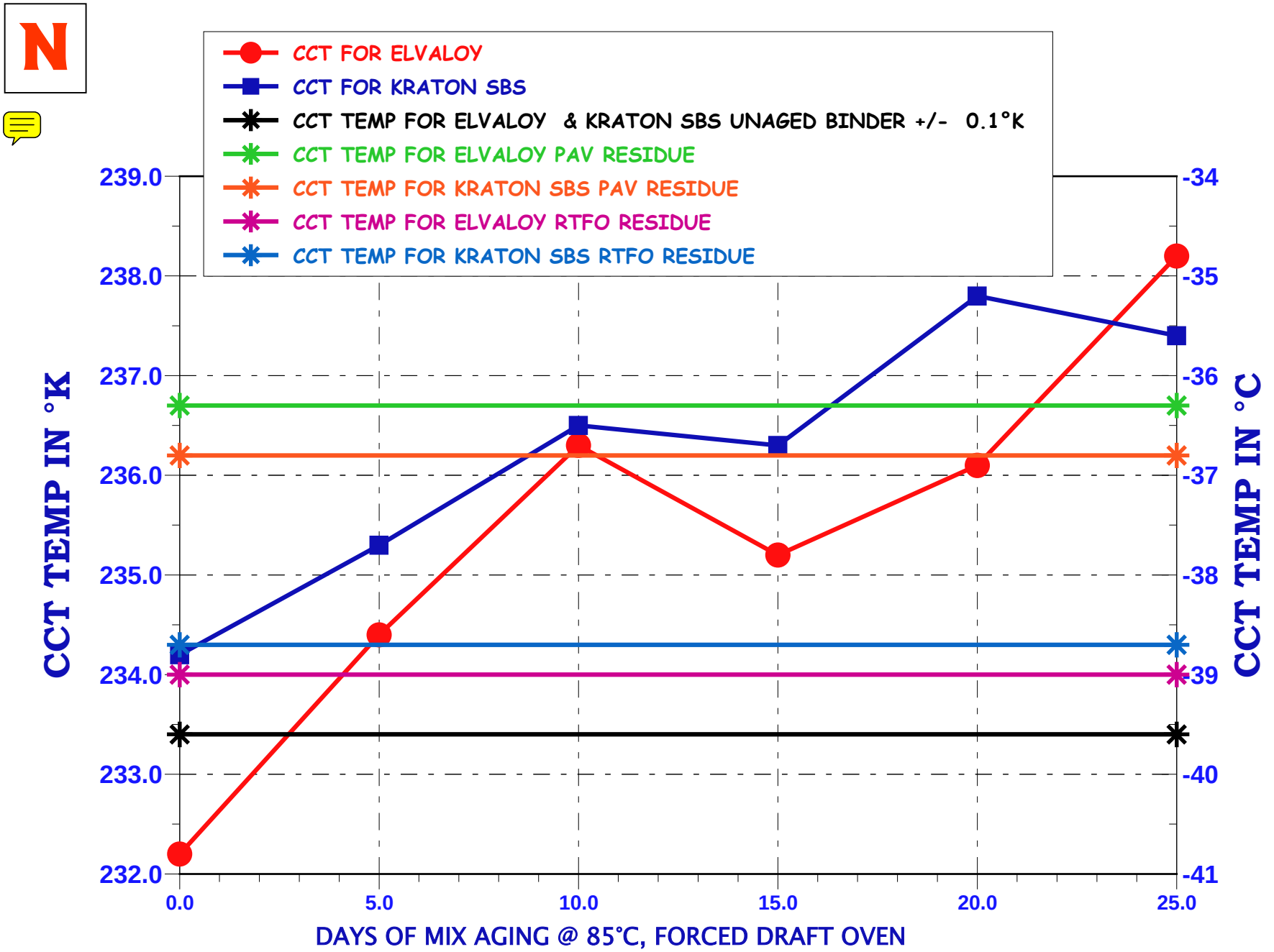


COMPARISON OF FATIGUE FAILURE BETWEEN PG 64-28 POLYMER MODIFIED AND PG 64-28 ACID REACTED

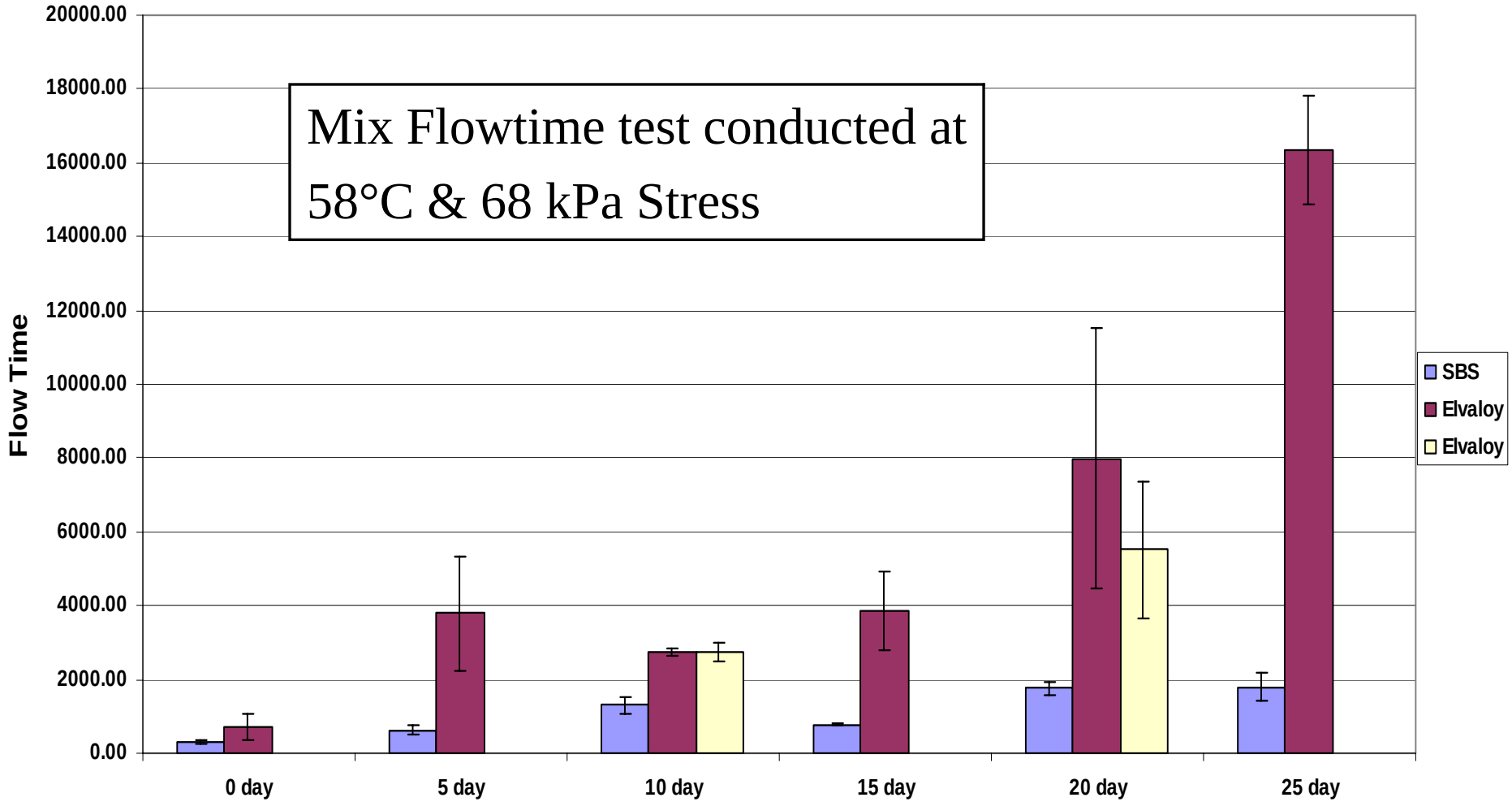


AGING COMPARISON OF SBS WITHOUT ACID & ELVALOY WITH ACID CATALYST AGGREGATE USED WAS A CRUSHED GRANITE




CCT FOR ELVALOY
CCT FOR KRATON SBS
CCT TEMP FOR ELVALOY & KRATON SBS UNAGED BINDER +/- 0.1°K
CCT TEMP FOR ELVALOY PAV RESIDUE
CCT TEMP FOR KRATON SBS PAV RESIDUE
CCT TEMP FOR ELVALOY RTFO RESIDUE
CCT TEMP FOR KRATON SBS RTFO RESIDUE
239.0
238.0
237.0
236.0
235.0
234.0
233.0
232.0
-34
-35
-36
-37
-38
-39
-40
-41
0.0
5.0
10.0
15.0
20.0
25.0
CCT TEMP IN °K
CCT TEMP IN °C
DAYS OF MIX AGING @ 85°C, FORCED DRAFT OVEN

MIX FLOWTIME TO FAILURE
RELATED TO DAYS OF MIX AGING @ 85°C IN FORCED DRAFT OVEN

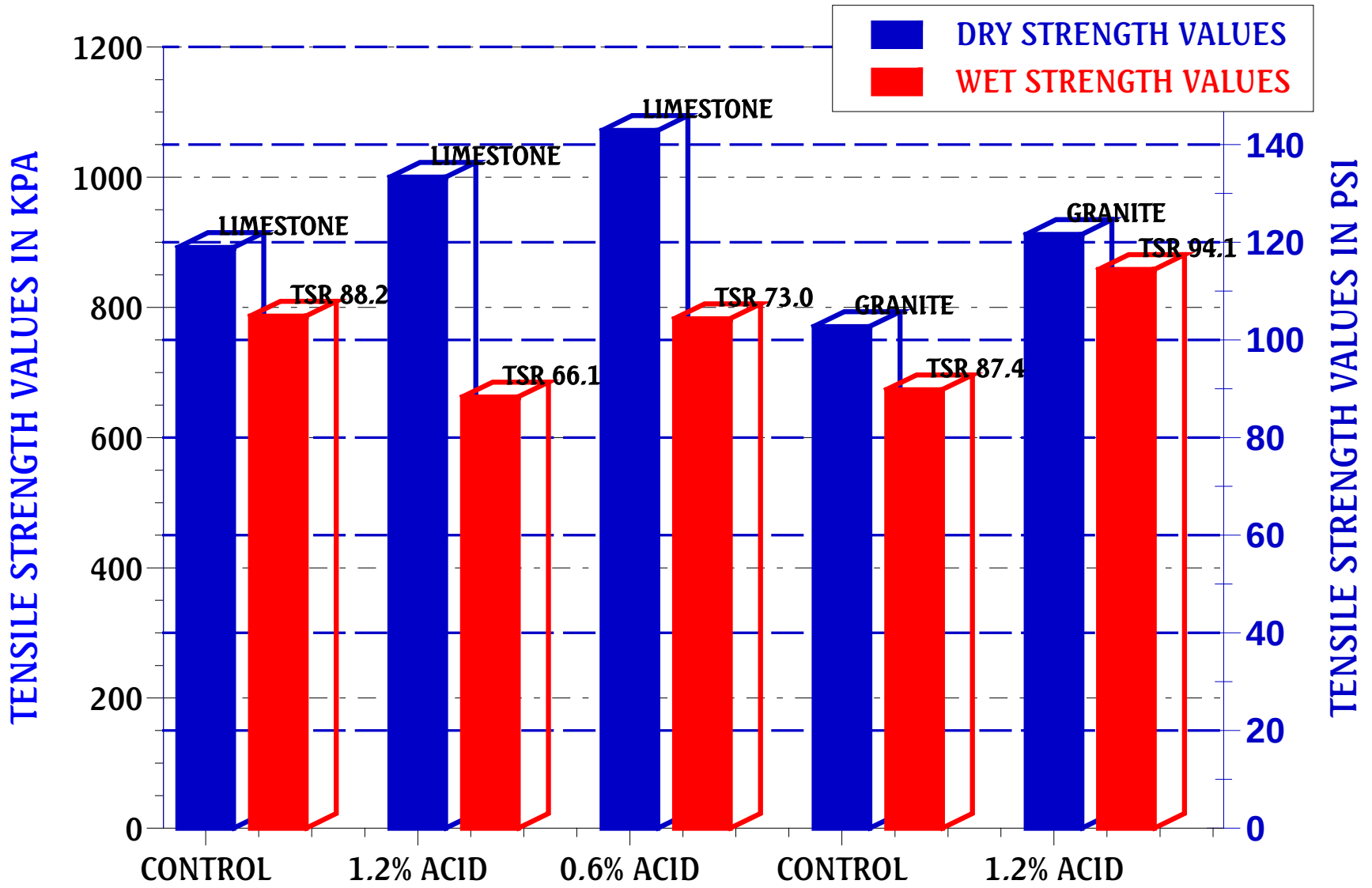


IMPACT OF MOISTURE ON

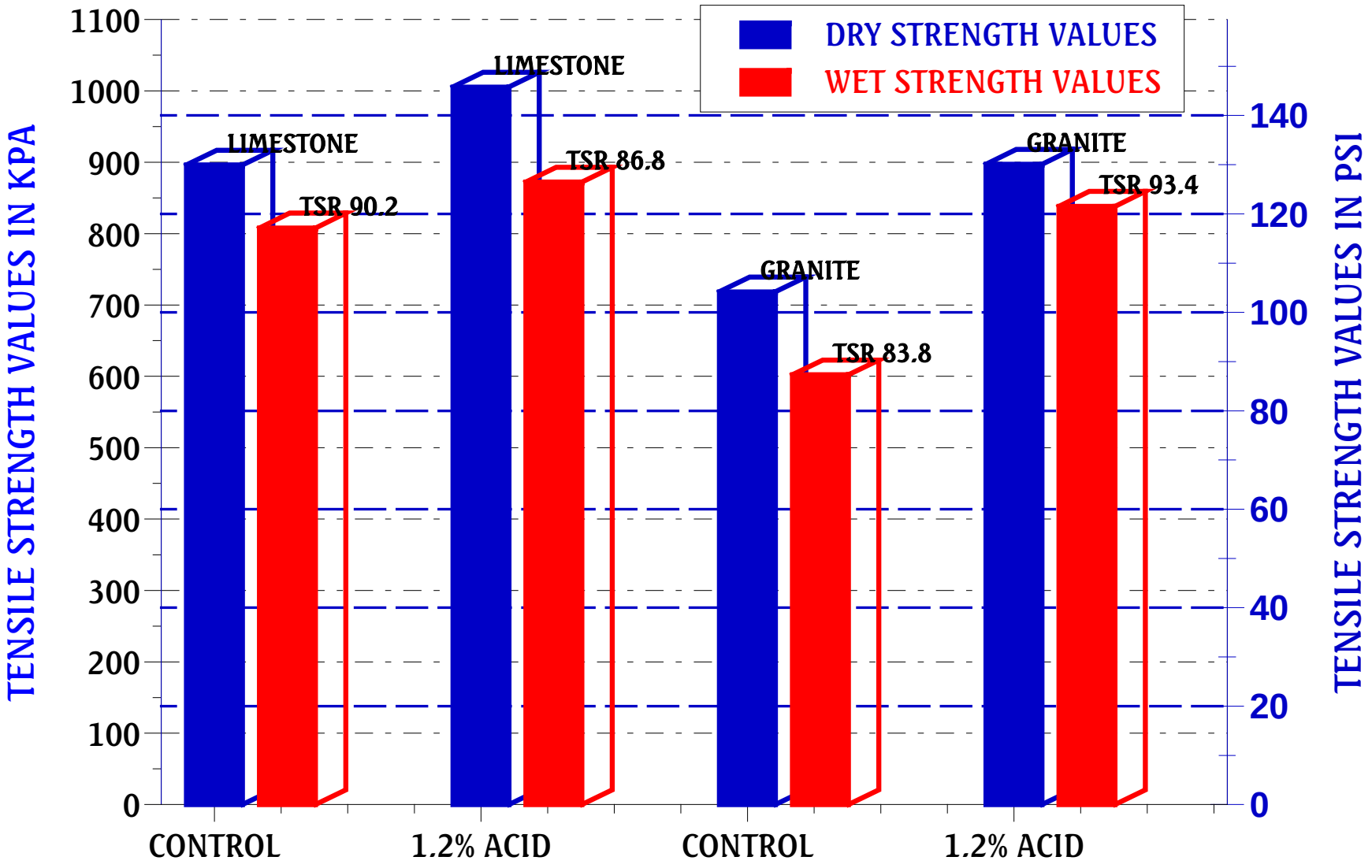
1. ACID MODIFIED ASPHALT
2. POLYMER MODIFIED + ACID
3. BLENDS CONTAINING PHOSPHATE ESTER ANTI-STRIP ADDITIVE

T-283 AND HAMBURG DATA

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

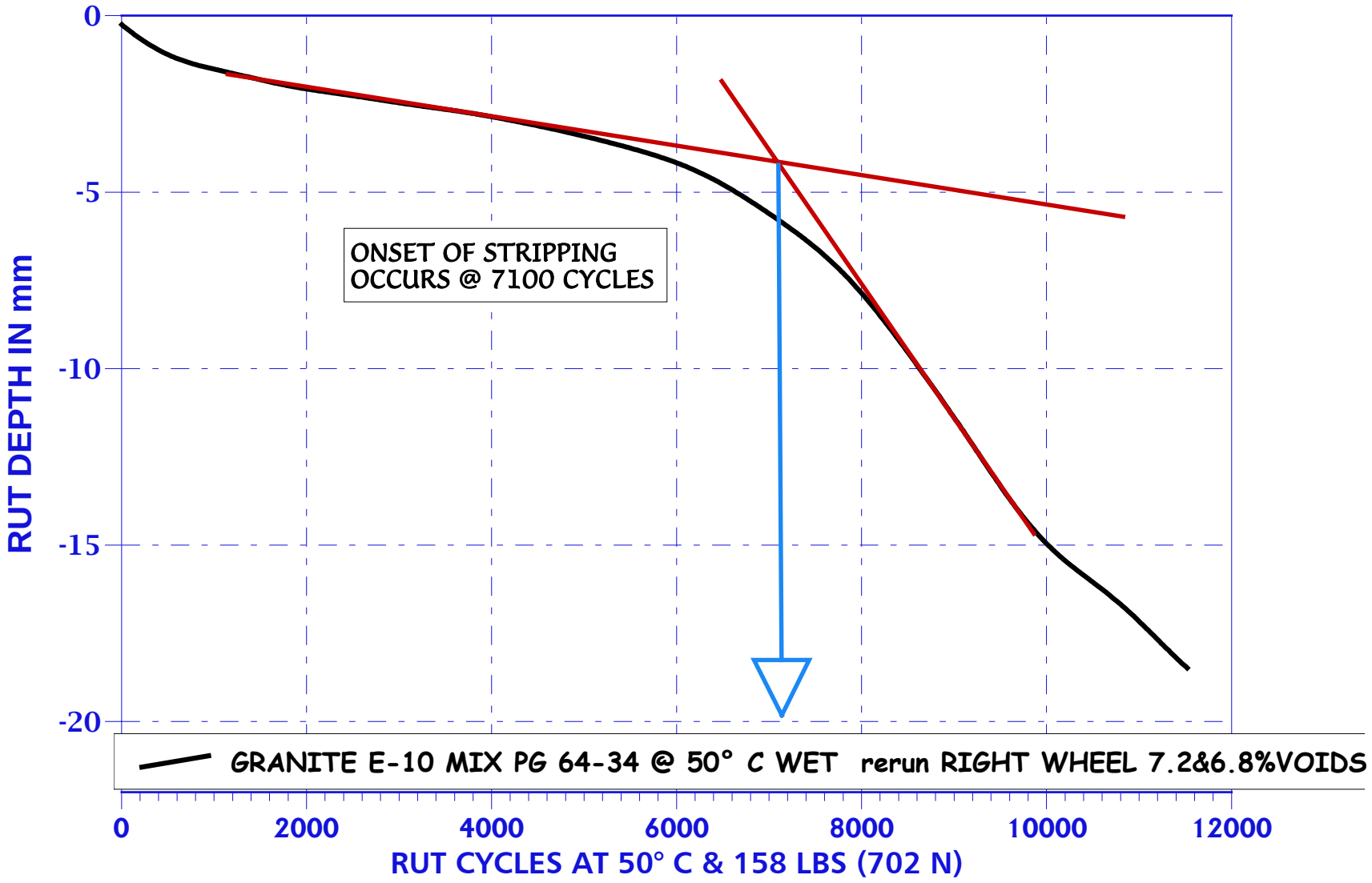


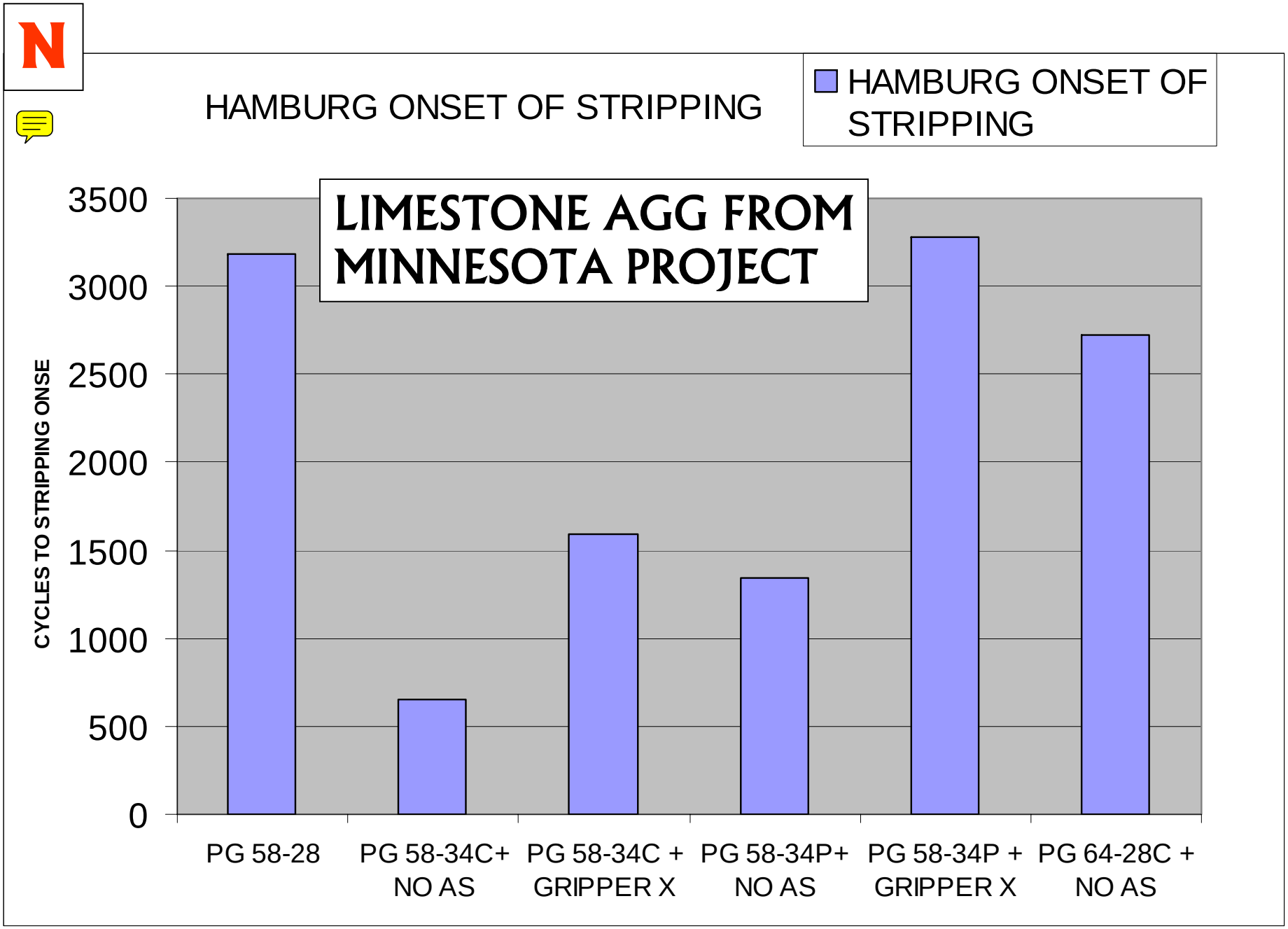
TENSILE STRENGTH TEST RESULTS FOR SOURCE B 64-22 AND SOURCE B 64-22 + 1.2% POLYPHOSPHORIC ACID USING LIMESTONE AND GRANITE MIXES



CLICK ON SLIDE TO RUN VIDEO

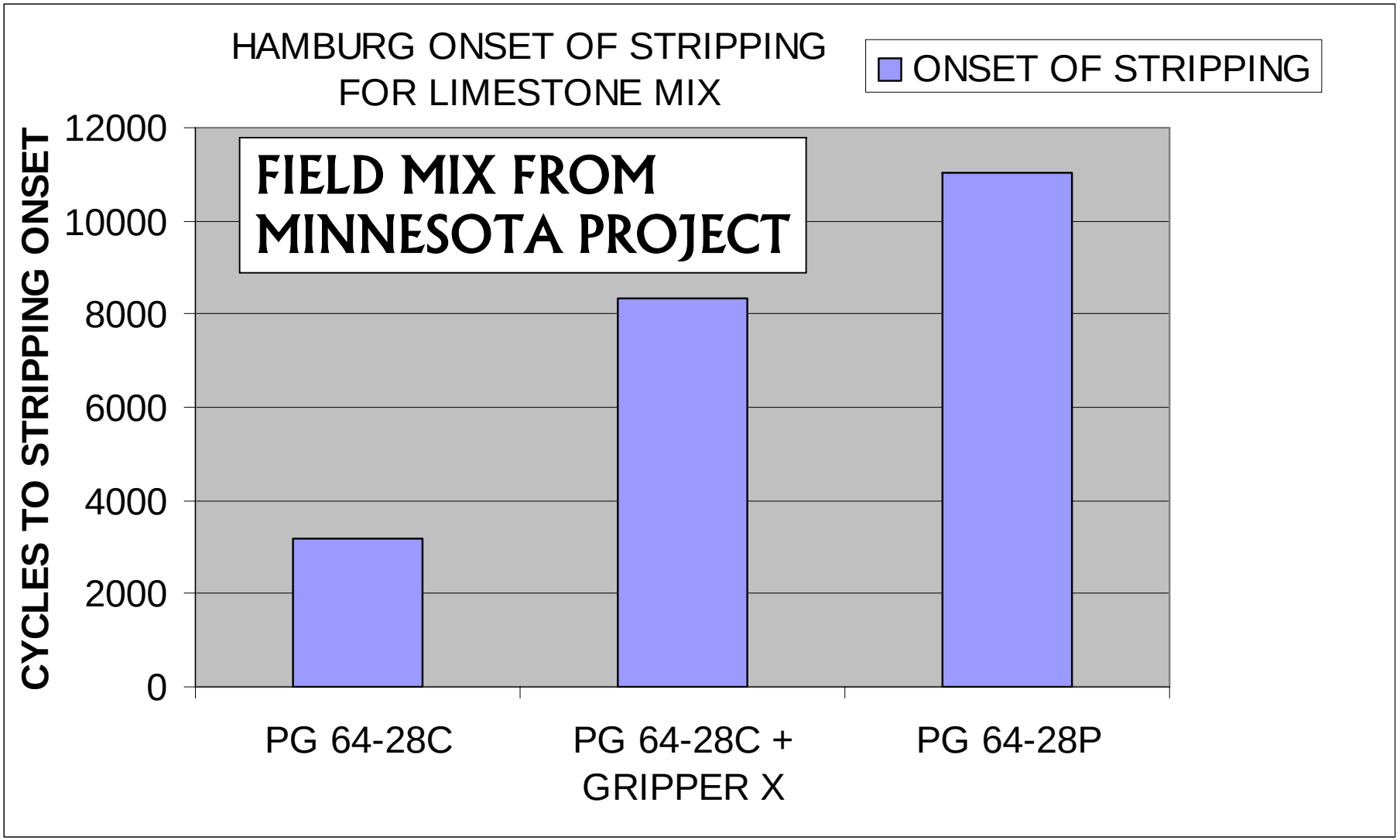
MATHY RUT TEST WITH PG 64-34 TESTED IN PMW HAMBURG WET AT 50° C



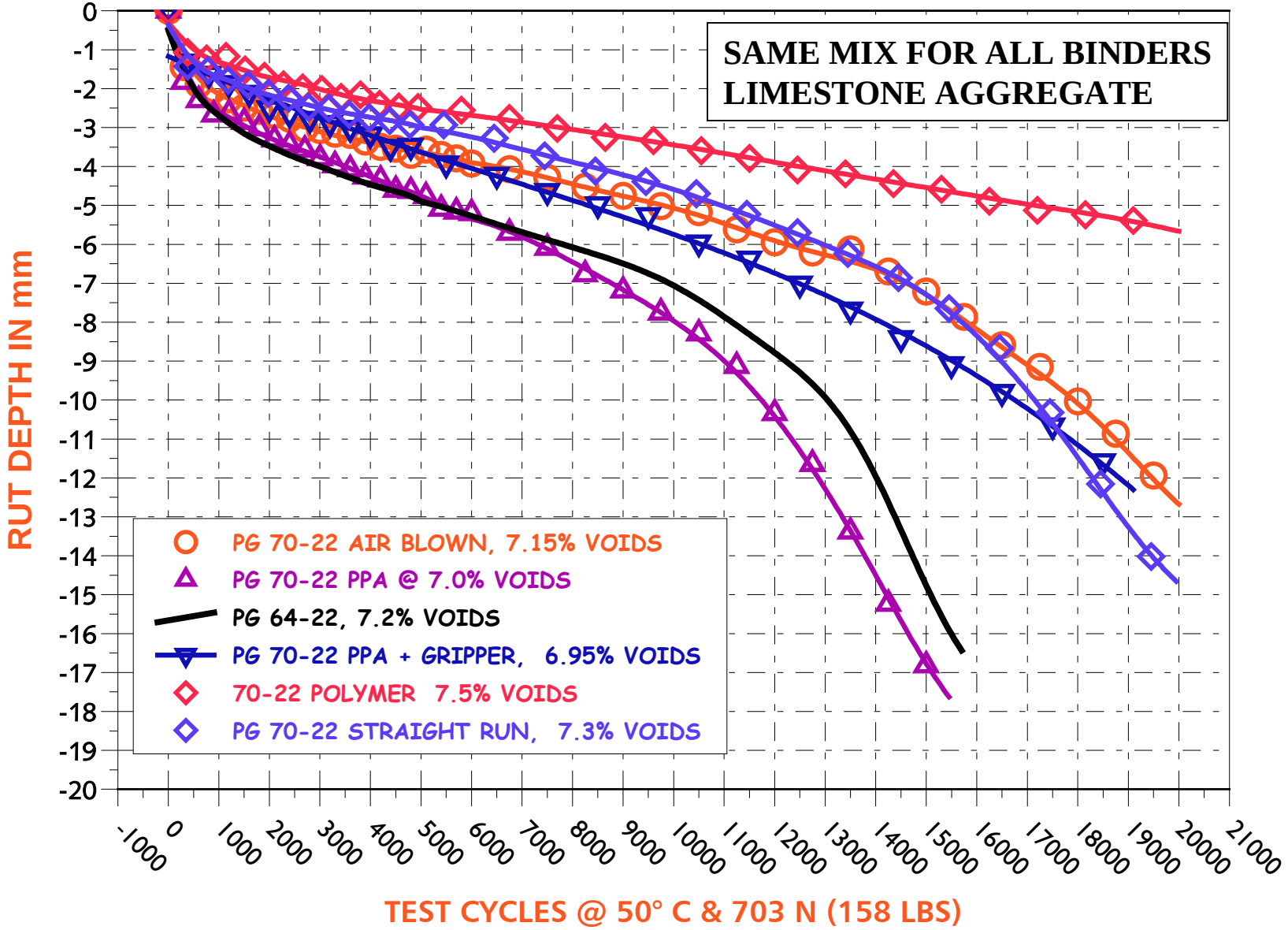

HAMBURG ONSET OF STRIPPING
HAMBURG ONSET OF STRIPPING
LIMESTONE AGG FROM MINNESOTA PROJECT
CYCLES TO STRIPPING ONSE
3500
3000
2500
2000
1500
1000
500
0
PG 58-28
PG 58-34C+ NO AS
PG 58-34C + GRIPPER X
PG 58-34P+ NO AS
PG 58-34P + GRIPPER X
PG 64-28C + NO AS

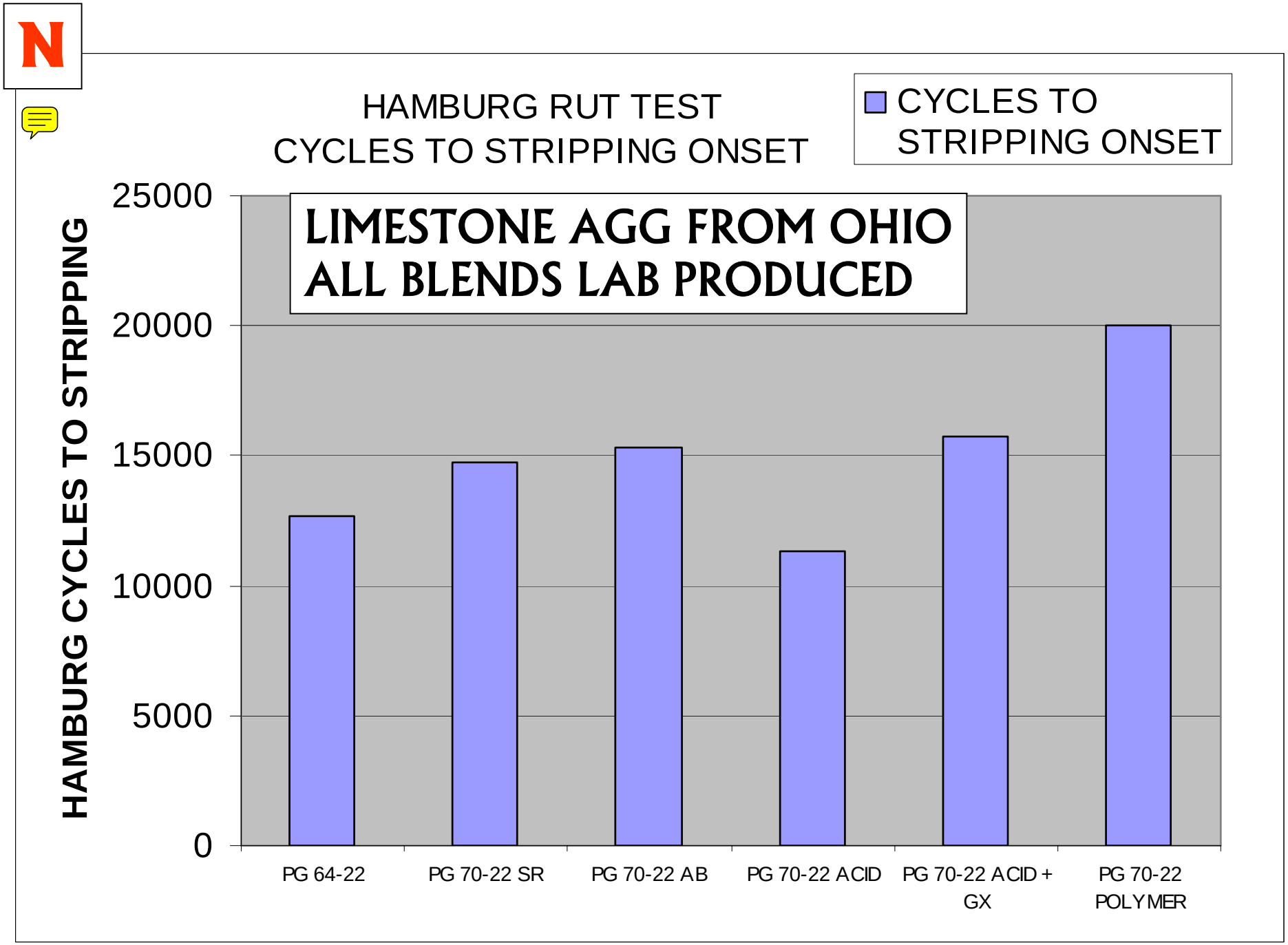

N
PG 58-34 ACID MODIFIED
4.5 MILES, PAVED JULY 2002
FEB 26 2004

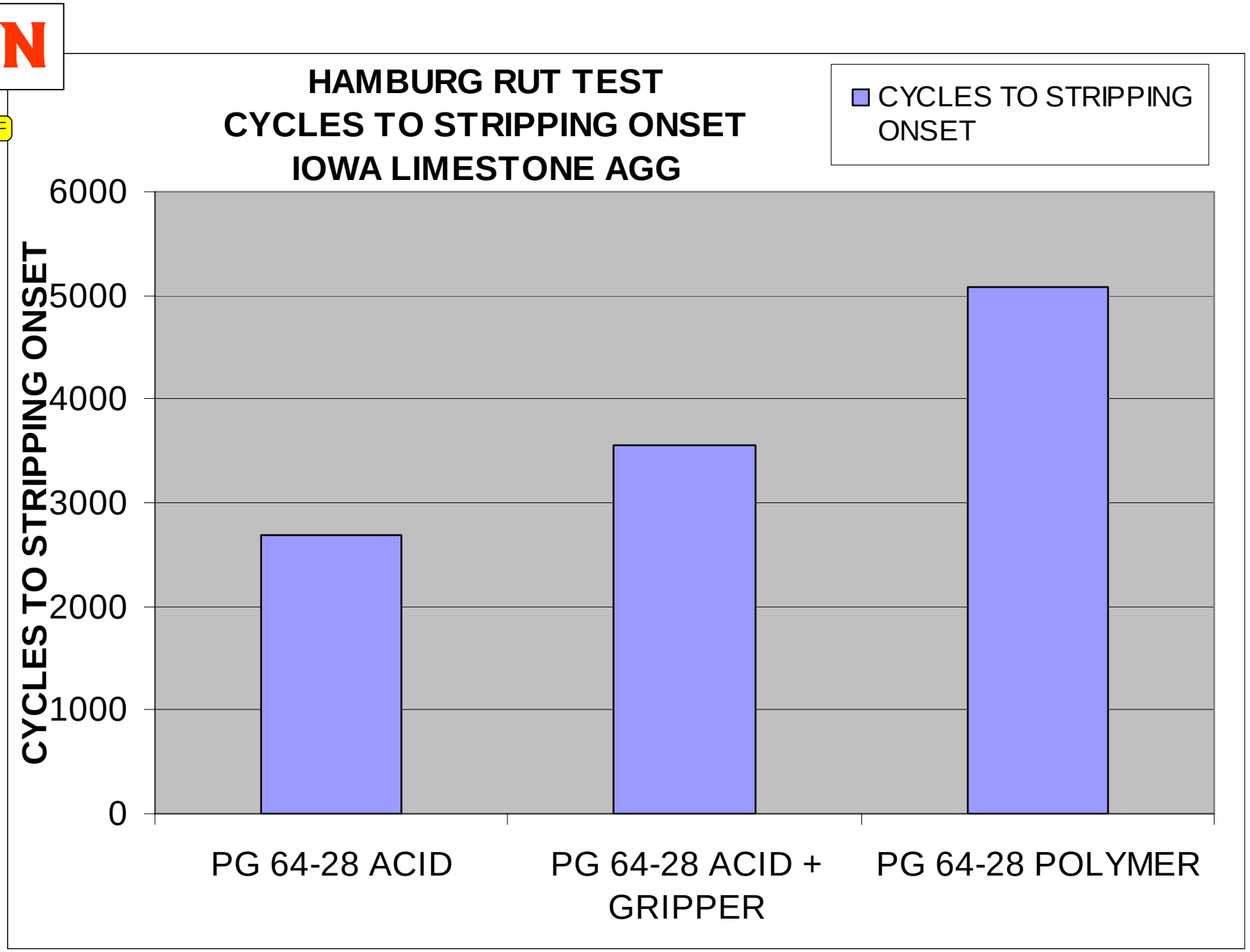

FEB 26 2004


HAMBURG ONSET OF STRIPPING
FOR LIMESTONE MIX
ONSET OF STRIPPING
FIELD MIX FROM
MINNESOTA PROJECT
CYCLES TO STRIPPING ONSET
12000
10000
8000
6000
4000
2000
0
PG 64-28C
PG 64-28C +
GRIPPER X
PG 64-28P

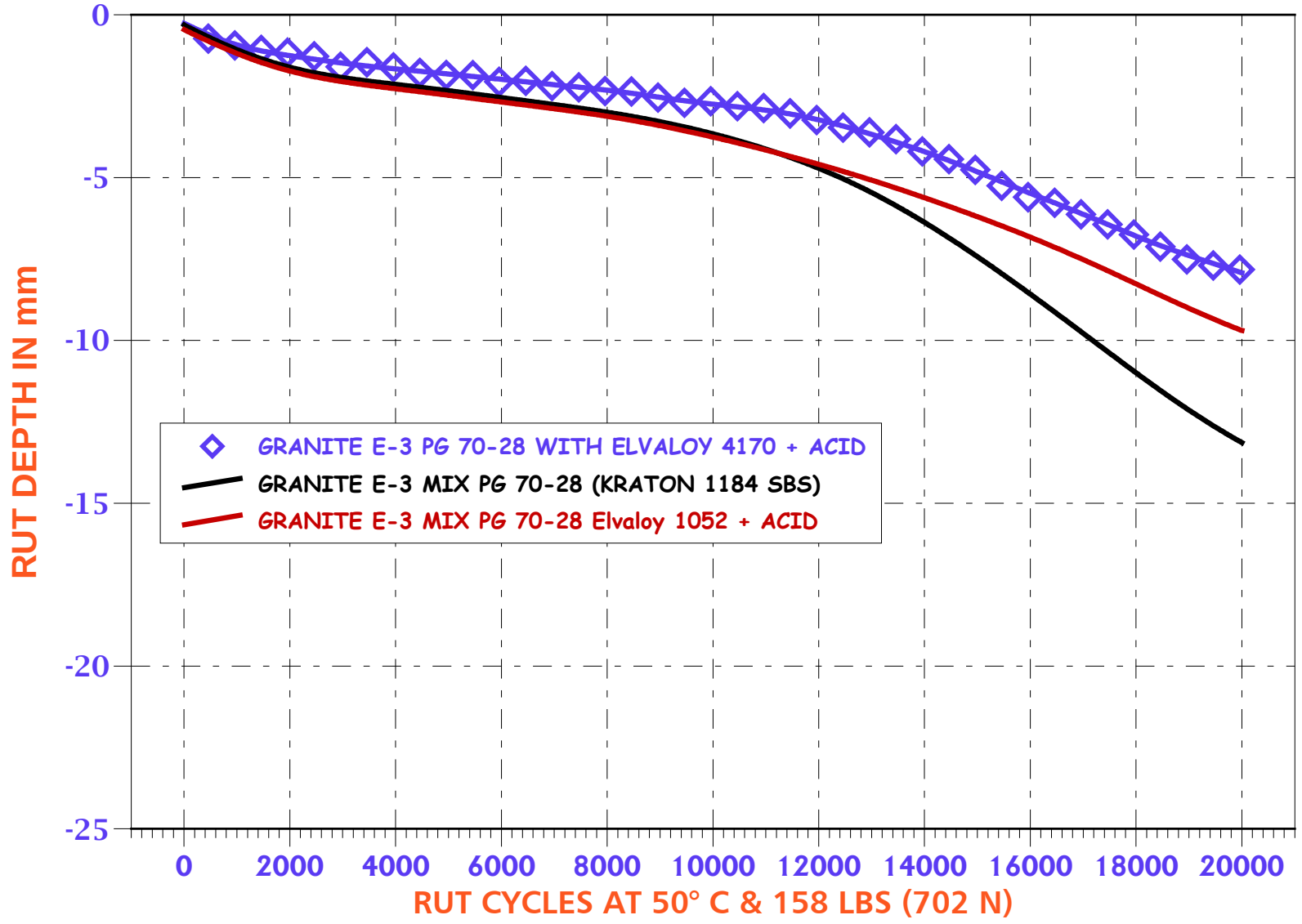
PMW HAMBURG RUT TEST OF PG 70-22 AND PG 64-22 BINDERS-- 70-22 AB, 70-22 PPA, 70-22 PPA + GRIPPER, 70-22 STRAIGHT RUN & 70-22 PMA




HAMBURG RUT TEST
CYCLES TO STRIPPING ONSET
CYCLES TO STRIPPING ONSET
LIMESTONE AGG FROM OHIO
ALL BLENDS LAB PRODUCED
HAMBURG CYCLES TO STRIPPING
25000
20000
15000
10000
5000
0
PG 64-22
PG 70-22 SR
PG 70-22 AB
PG 70-22 ACID
PG 70-22 ACID + GX
PG 70-22 POLYMER


HAMBURG RUT TEST
CYCLES TO STRIPPING ONSET
IOWA LIMESTONE AGG
CYCLES TO STRIPPING ONSET
CYCLES TO STRIPPING ONSET
6000
5000
4000
3000
2000
1000
0
PG 64-28 ACID
PG 64-28 ACID + GRIPPER
PG 64-28 POLYMER

RUT TEST GRANITE E-3 MIX & PG 70-28
TESTED WET AT 50° C



"When you have eliminated the impossible, whatever remains, however improbable, must be the truth."

Arthur Conan Doyle

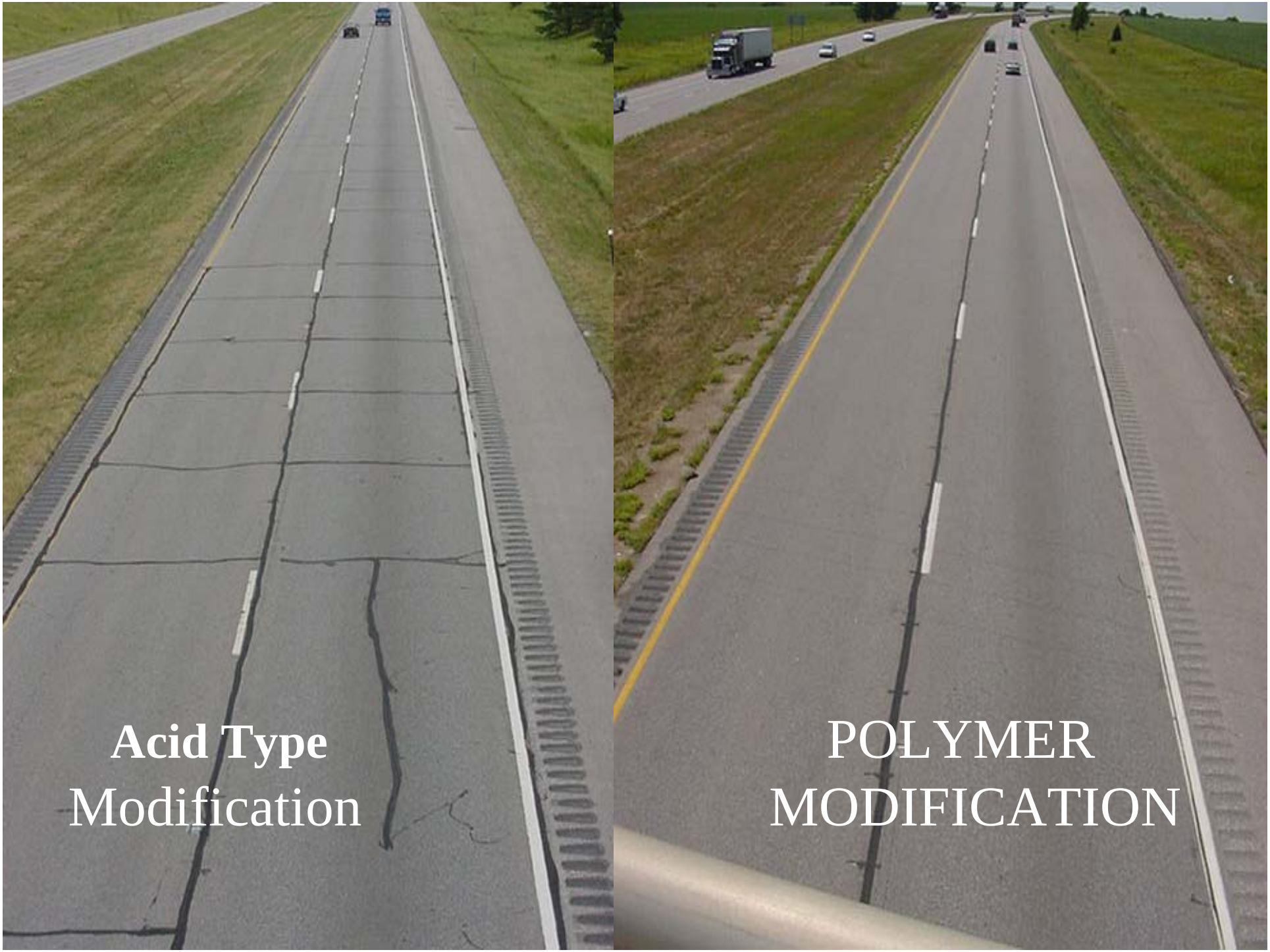
NEBRASKA I-80 CRACKING

COMPARISON OF PG 70-28 MADE WITH STYLINK & 70-28 MADE WITH ELVALOY + ACID

CONSTRUCTED 1999, SOME OF THE FIRST SUPERPAVE PROJECTS IN NEBRASKA

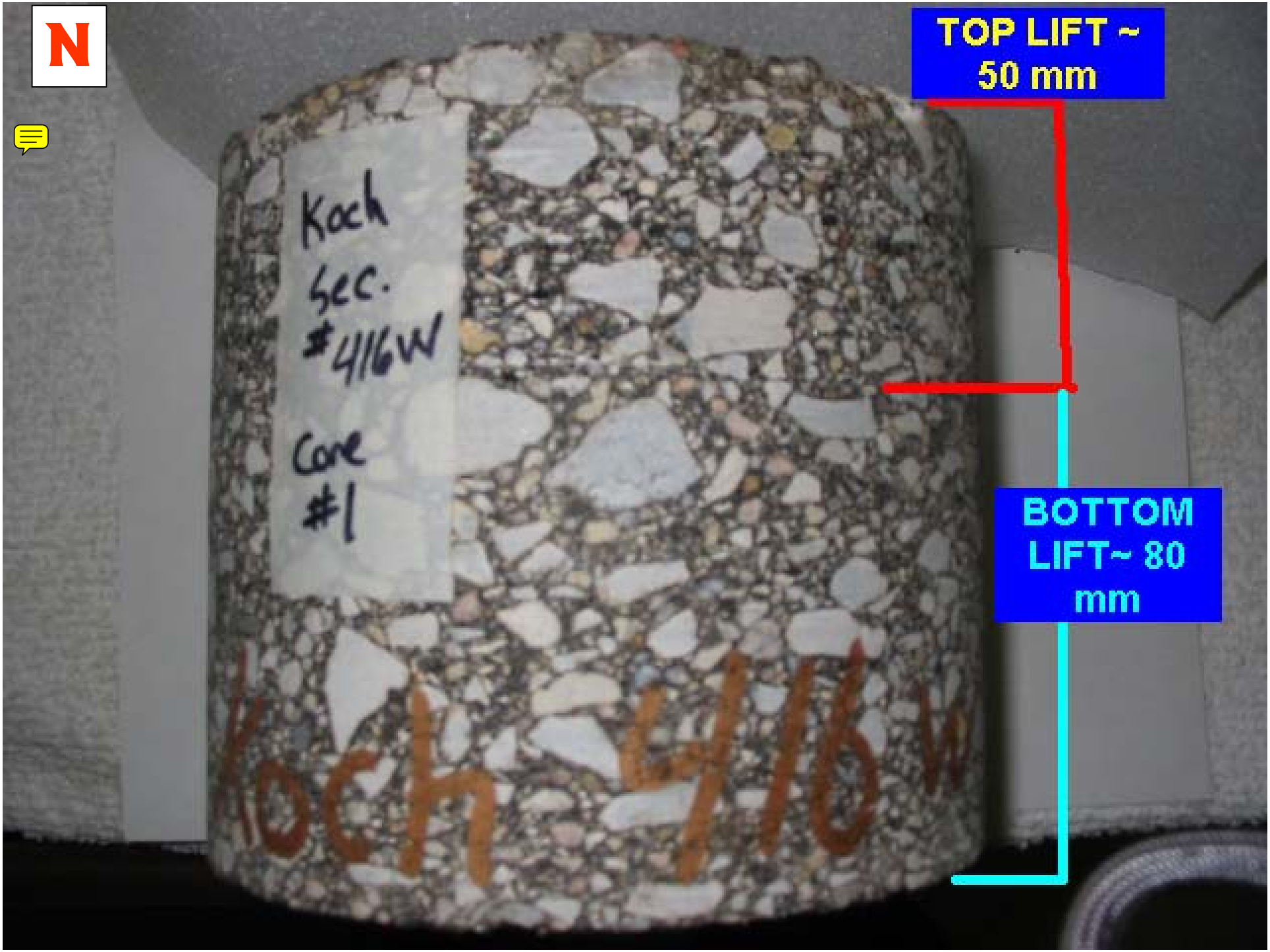
EXTENSIVE CRACKING IN ELVALOY + ACID SECTIONS &MINIMAL CRACKING IN STYLINK SECTIONS

ACID MODIFICATION WAS BLAMED FOR THIS PROBLEM


Acid Type
Modification
POLYMER
MODIFICATION

TO INVESTIGATE THIS PROBLEM CORES WERE CUT FROM BOTH THE STYLINK AND ELVALOY+ACID SECTIONS. ONE PORTION OF THE ELVALOY + ACID SECTIONS DID NOT EXHIBIT ANY CRACKING AND CORES WERE TAKEN FROM THIS LOCATION AS WELL.

THE PROJECT CONSISTED OF A 80 mm BOTTOM LIFT AND A 50 mm TOP LIFT. BOTH LIFTS WERE CONSTRUCTED WITH THE SAME MIX AND BINDER


N
TOP LIFT ~ 50 mm
BOTTOM LIFT~ 80 mm
Koch
Sec.
#416W
Core
#1
Koch 416W

UNCRACKED SECTION

TOP LIFT ~ 50 mm

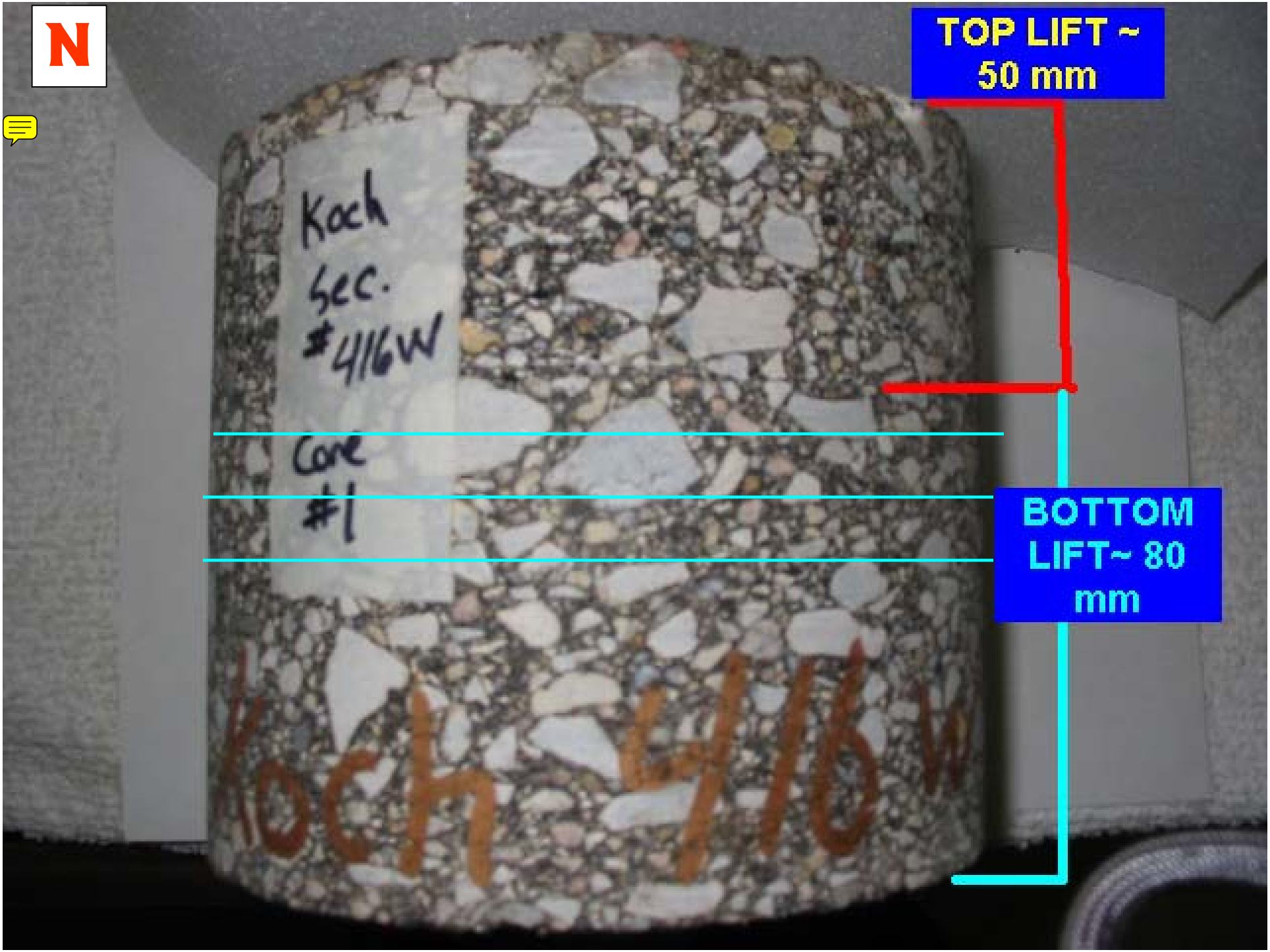
BOTTOM LIFT ~ 80 mm

PROPERTIES OF BINDER RECOVERED FROM TOP 2" OF IDENTIFIED CORES SHIPPED GRADE = PG 70-28

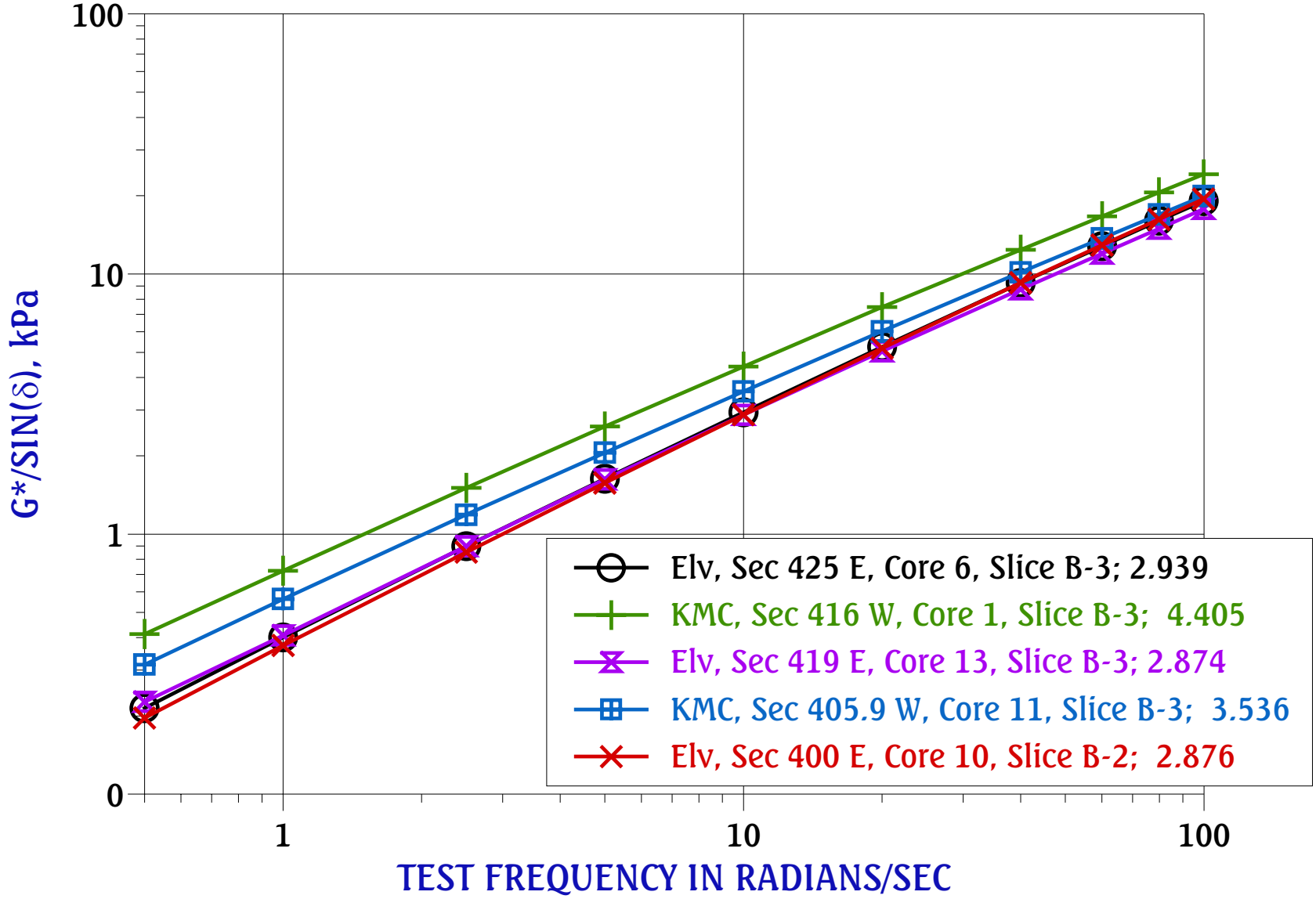
N

- Core 405.9W—Stylink, #11
- 2.2 kPa @ 79.4°C
- 5000 kPa @ 20° C
- @ -18°C
  - S=252 Mpa
  - M=0.306

- Core 425E—Elvaloy + acid, #3
- 2.2 kPa @ 77.2°C
- 5000 kPa @ 19.1° C
- @ -18°C
  - S=264 Mpa
  - M=0.324

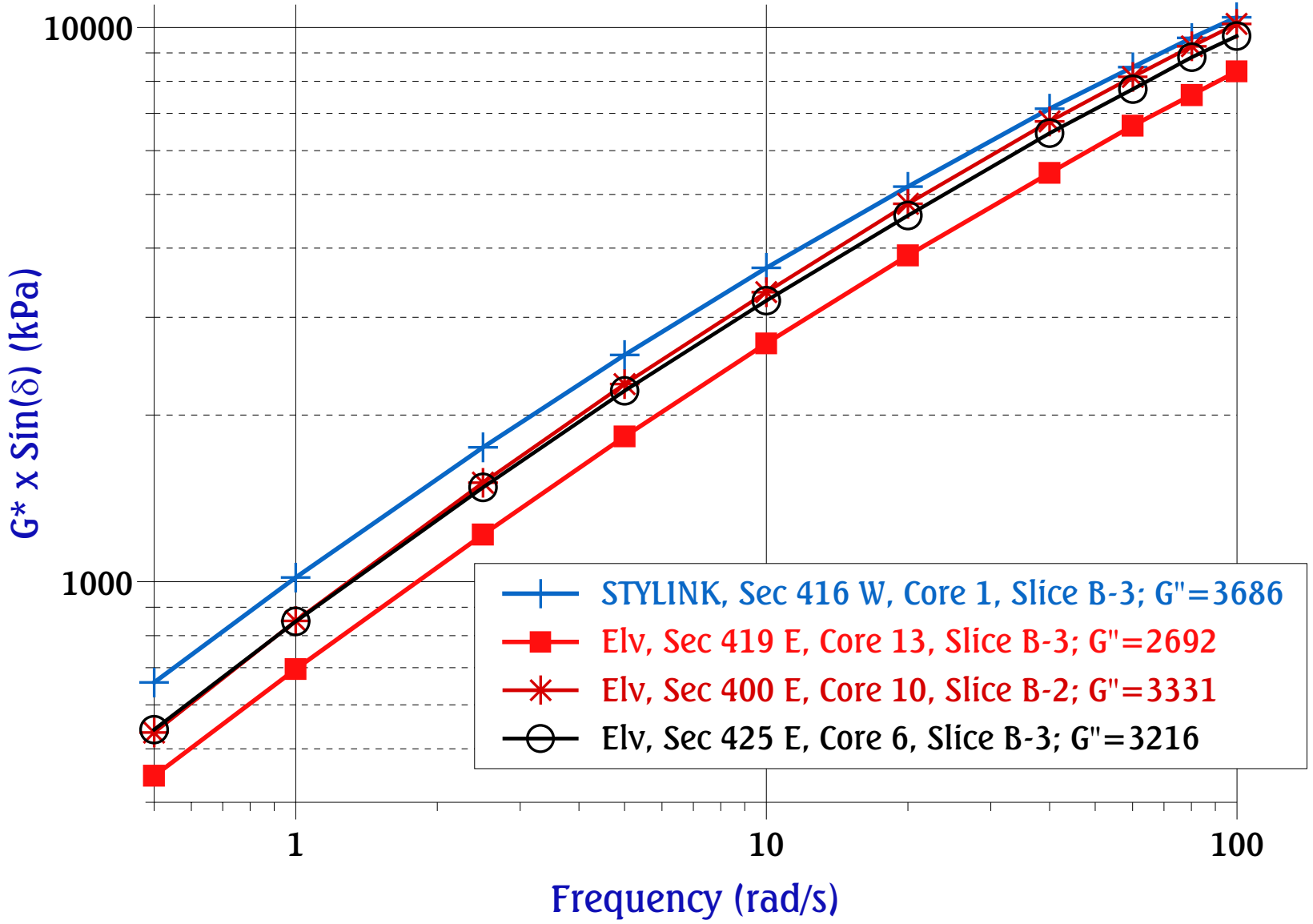

N
TOP LIFT ~ 50 mm
Koch
Sec.
#416W
Core
#1
BOTTOM LIFT~ 80 mm
Koch 416W

Nebraska I-80, Rec AC FROM BOTTOM LIFT
70°C Frequency Sweeps, G*/Sin(δ)

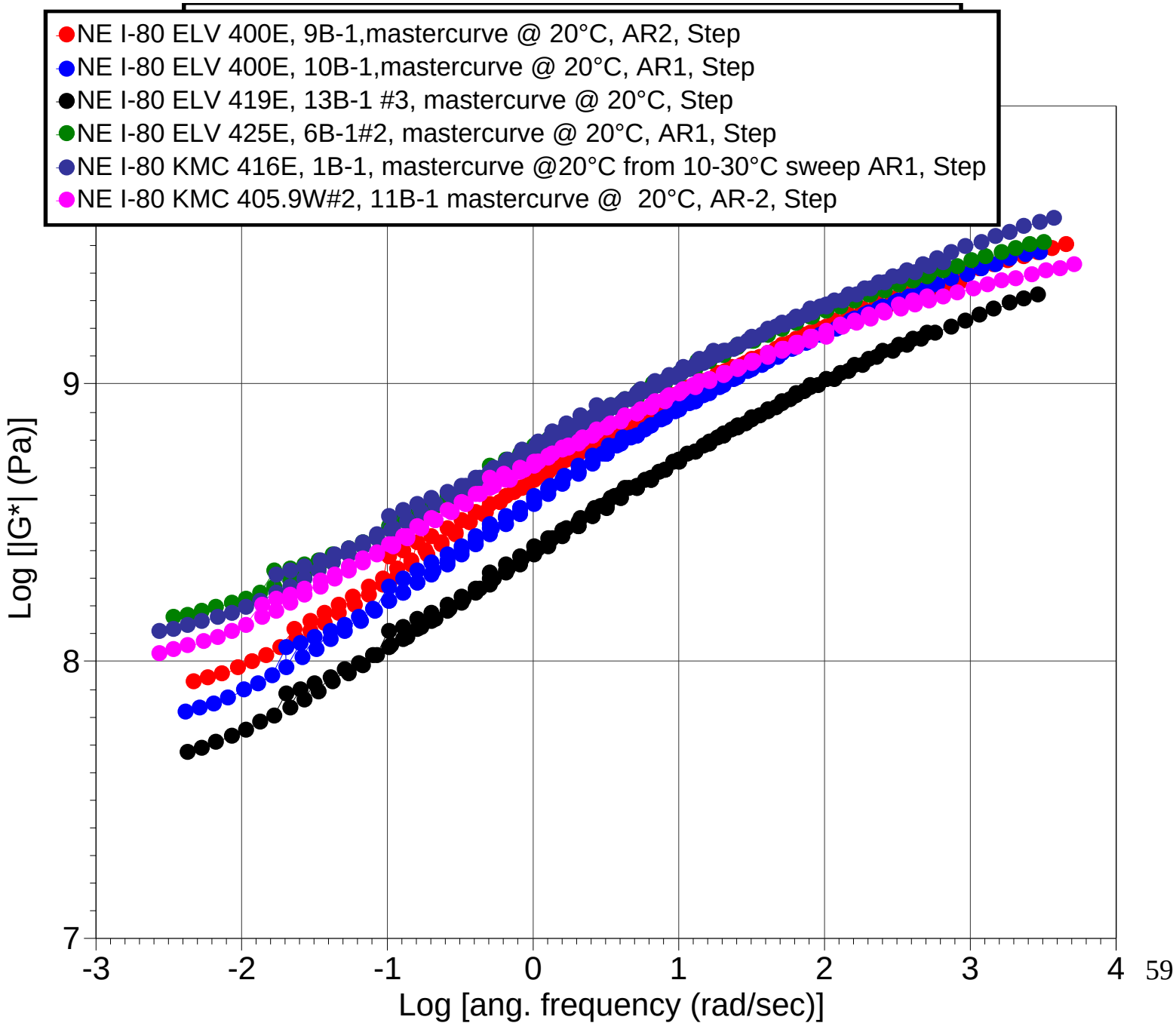


02/22/04 23:08:14 C:\DRIVE E\ATS PLOTIT 2004\Nebraska Project\70 C Frequency Sweeps BOTTOM LAYERS.spf

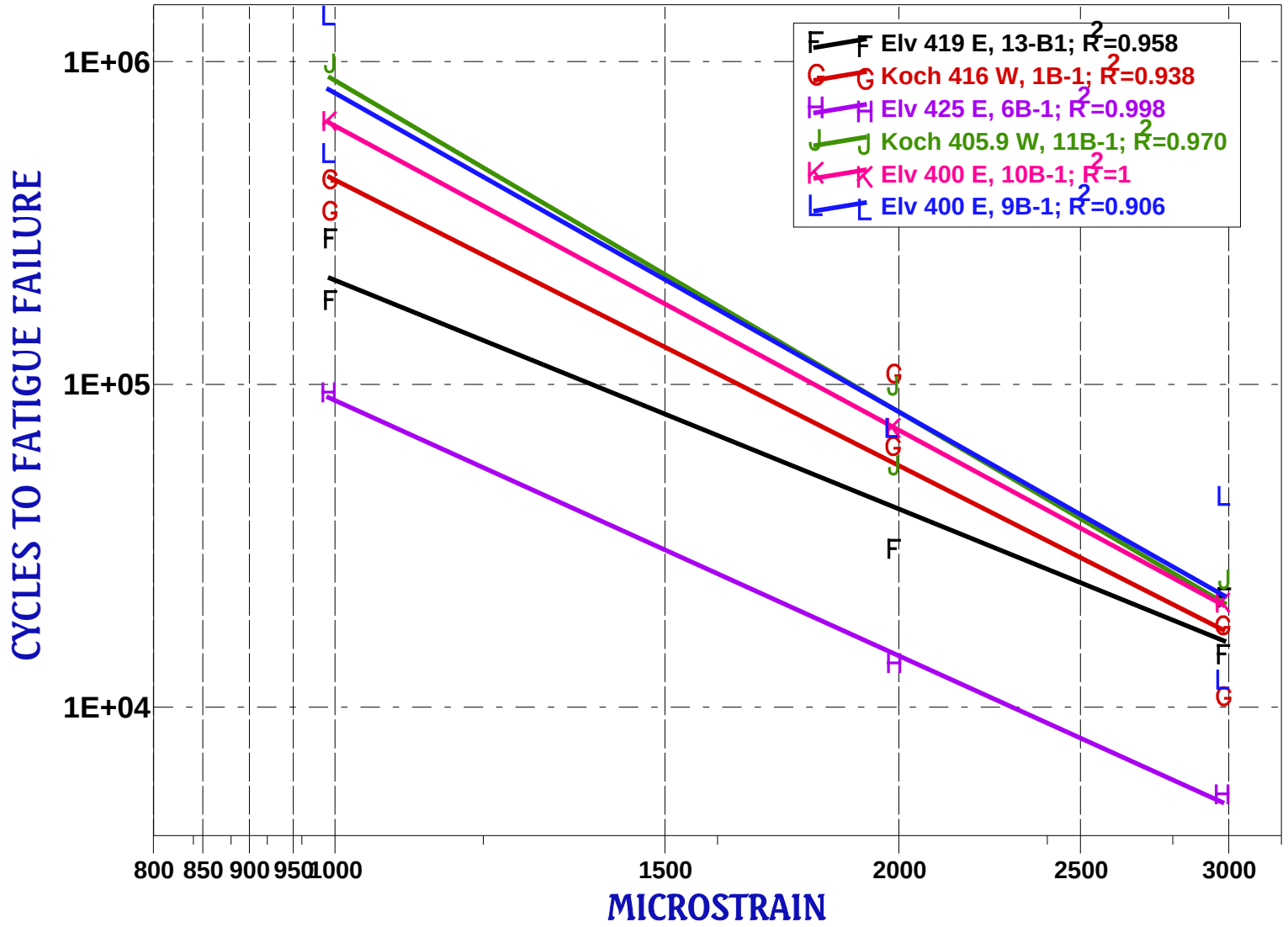
Nebraska I-80, Rec AC FROM BOTTOM LIFT
19°C Frequency Sweeps
G* x Sin(δ), kPa



02/22/04 21:55:50 C:\DRIVE E\ATS PLOTIT 2004\Nebraska Project\19 C Frequency Sweeps FOR BOTTOM LAYERS.spf

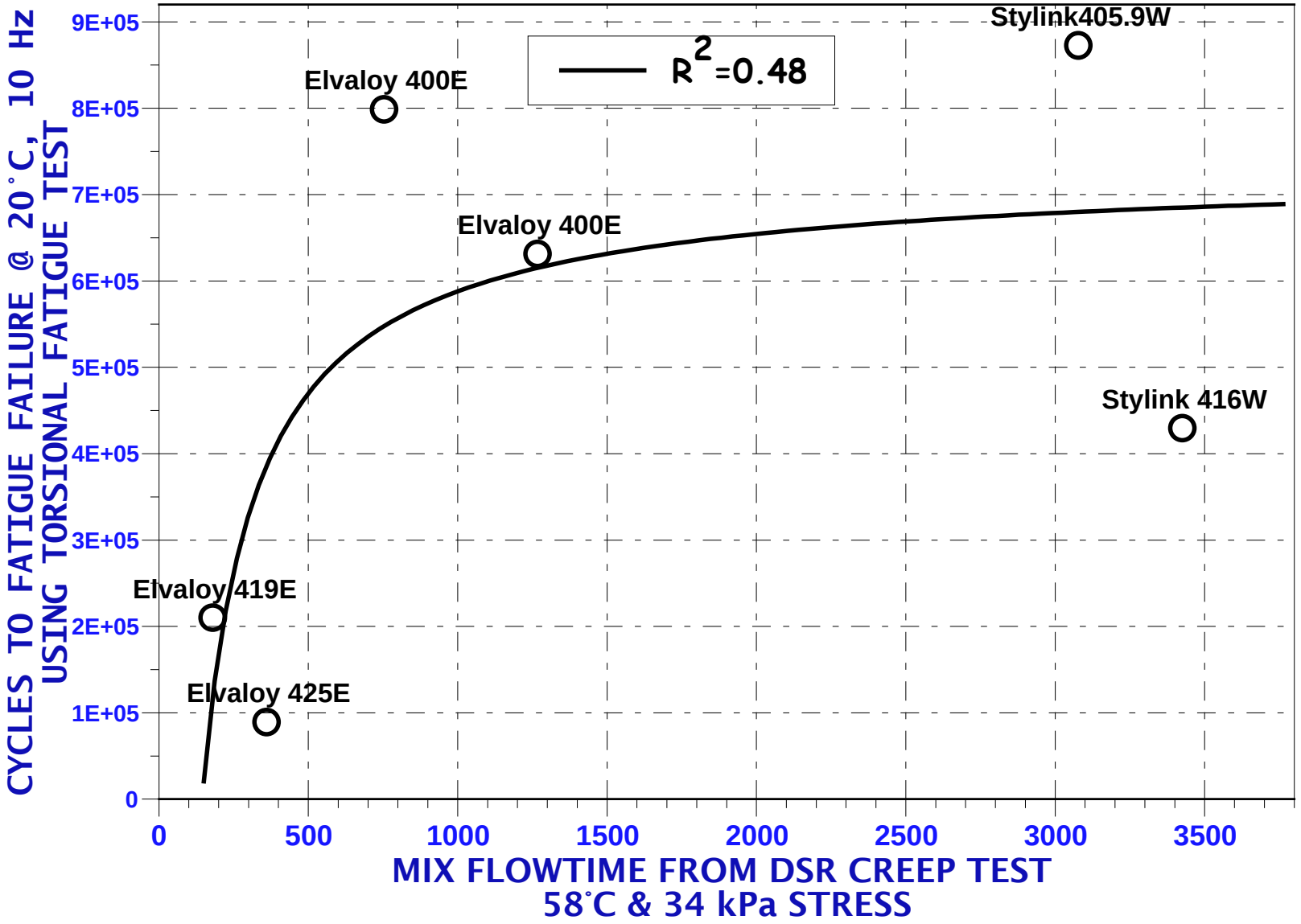

NE I-80 ELV 400E, 9B-1,mastercurve @ 20°C, AR2, Step
NE I-80 ELV 400E, 10B-1,mastercurve @ 20°C, AR1, Step
NE I-80 ELV 419E, 13B-1 #3, mastercurve @ 20°C, Step
NE I-80 ELV 425E, 6B-1#2, mastercurve @ 20°C, AR1, Step
NE I-80 KMC 416E, 1B-1, mastercurve @20°C from 10-30°C sweep AR1, Step
NE I-80 KMC 405.9W#2, 11B-1 mastercurve @ 20°C, AR-2, Step
Log [|G*| (Pa)]
9
8
7
-3
-2
-1
0
1
2
3
4
Log [ang. frequency (rad/sec)]

Nebraska I-80, FATIUGE EVALUATION OF BOTTOM LIFT SLICES

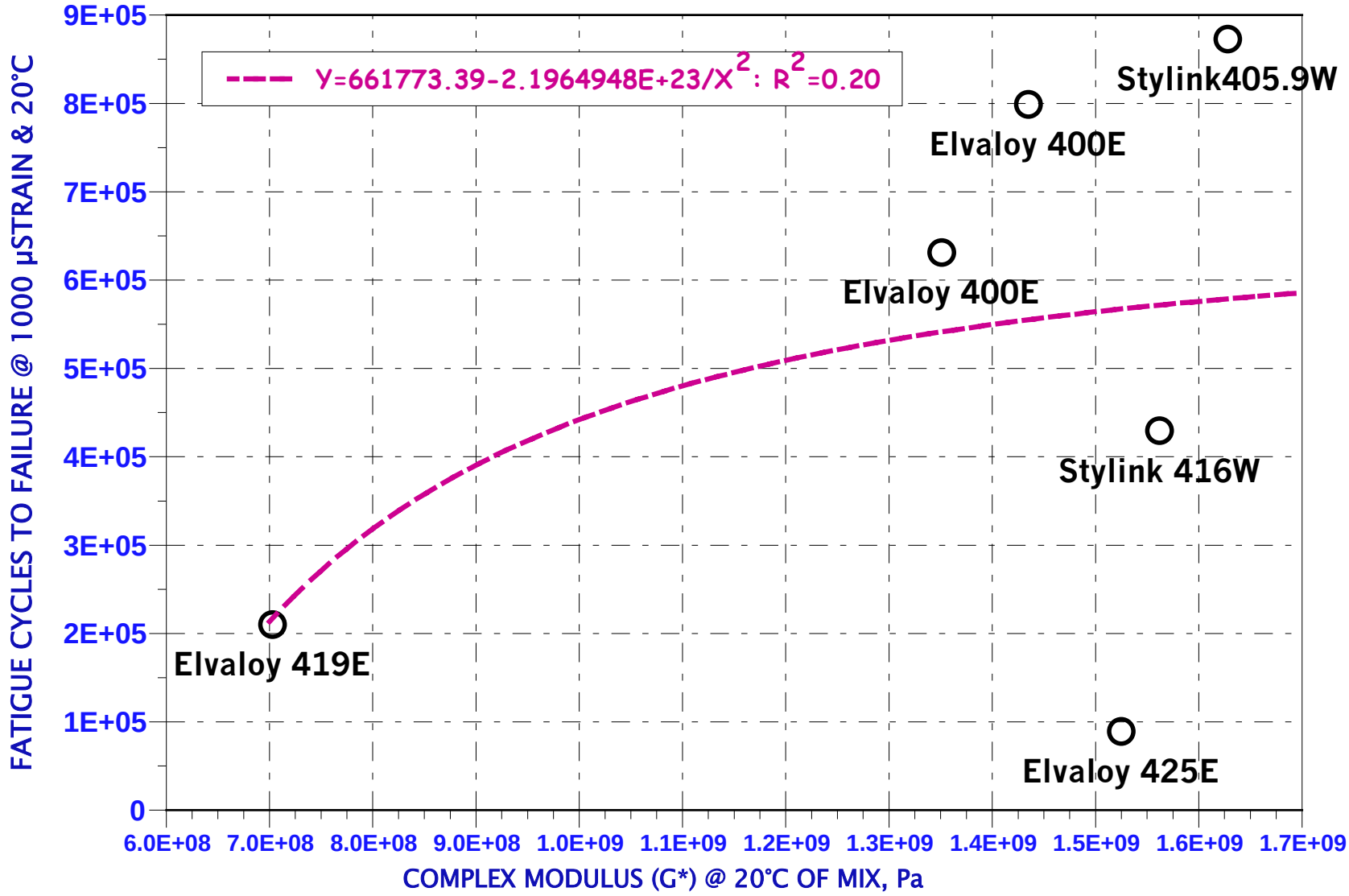


02/22/04 23:45:25 C:\DRIVE_E\(A)RHIOS600_2004\Nebraska Project\Nebraska I-80#1.spf

CYCLES TO FAILURE @ 20°C AS A FUNCTION OF MIX FLOWTIME TO FAILURE AT 58°C, 34 kPa STRESS

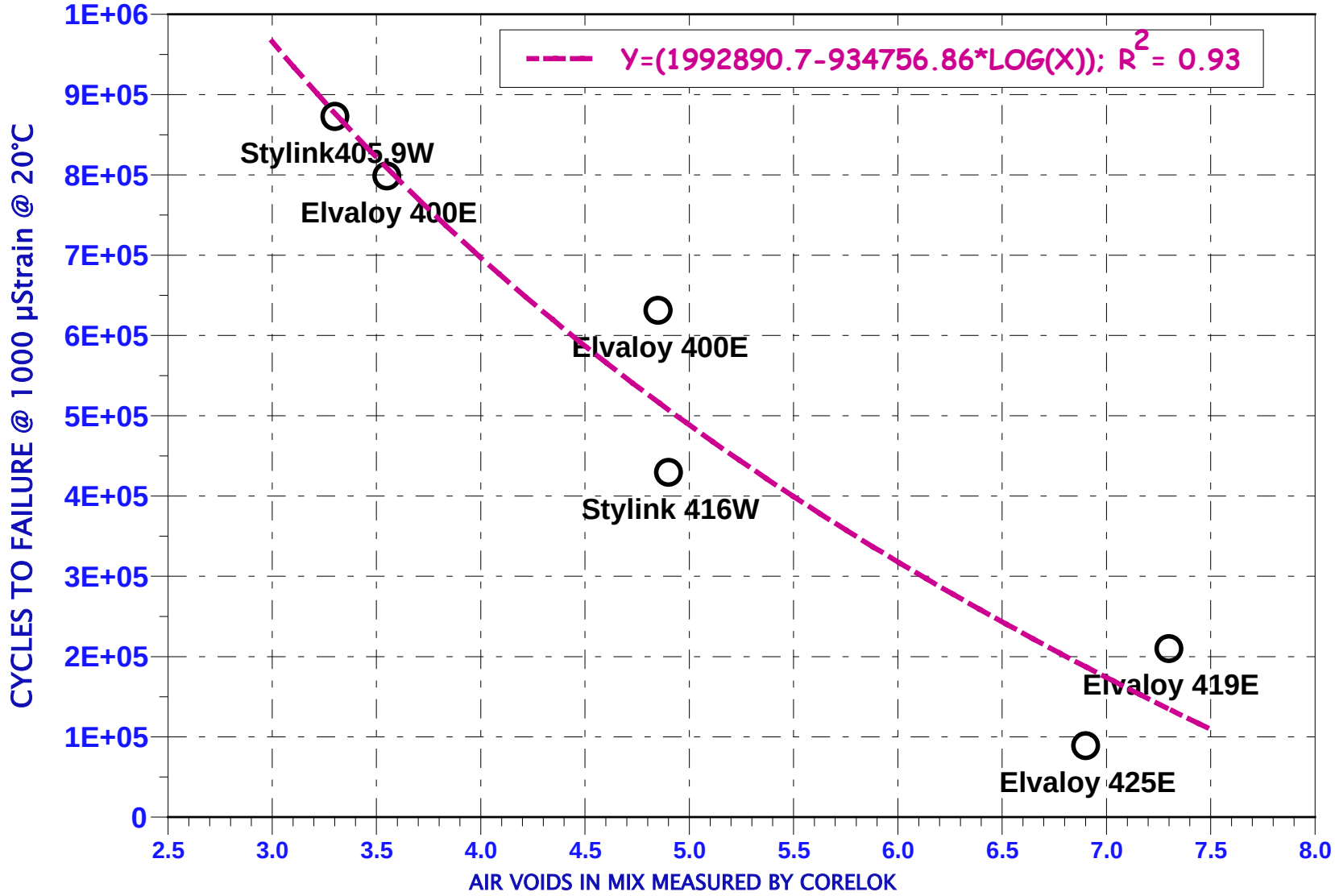


FATIGUE CYCLES TO FAILURE @ 1000 µSTRAIN & 20°C AS A FUNCTION OF COMPLEX MODULUS OF THE MIX TESTED AT 20°C



02/22/04 22:50:22 C:\DRIVE_E\AR2000\RESULTS\2004\NE I-80\CYCLES TO FAILURE @ 1000 MS = F(MIX G star @ 20C).spf

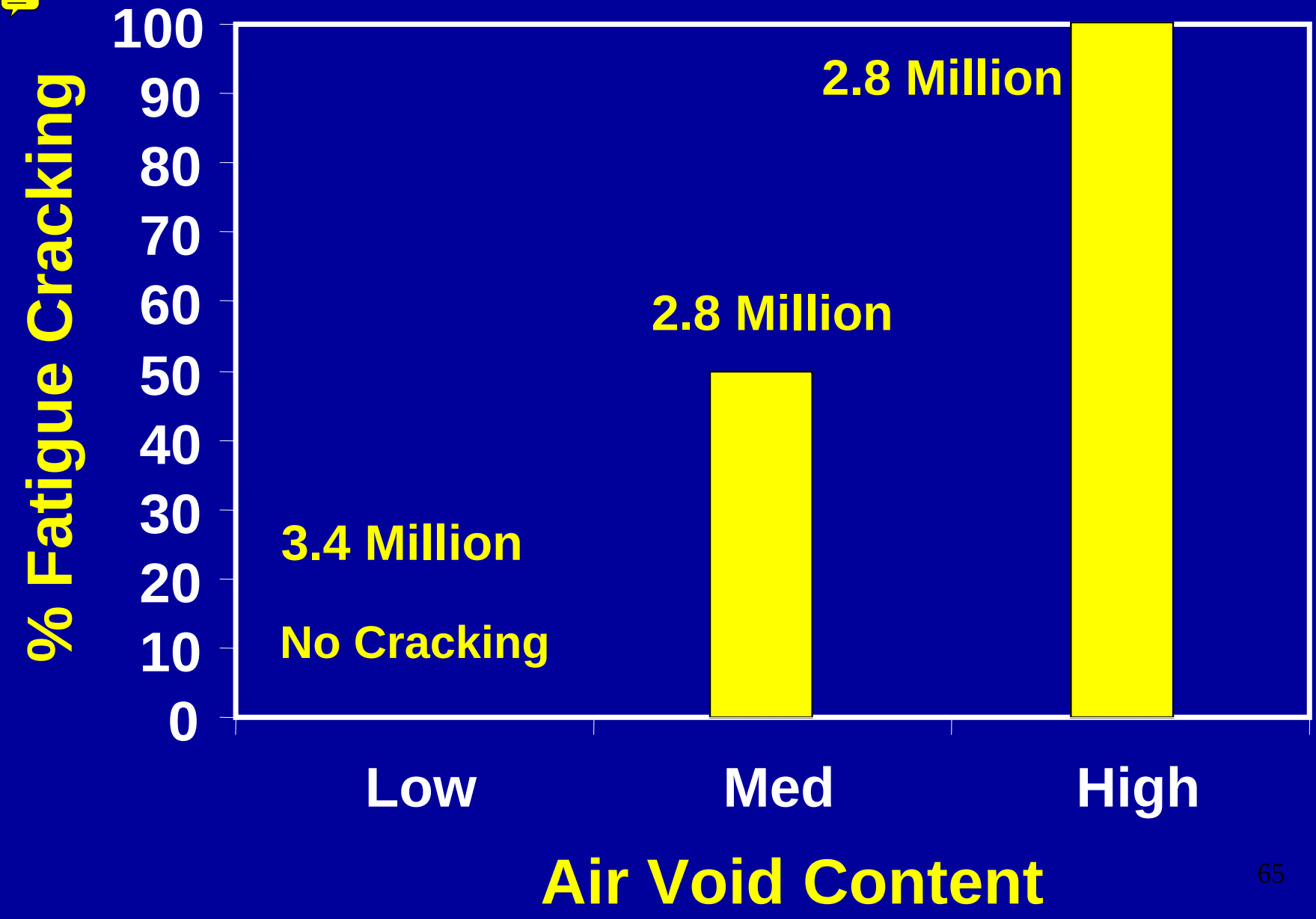
CYCLES TO FATIGUE FAILURE @ 1000 μSTRAIN AND 20°C AS A FUNCTION OF MIX AIR VOIDS



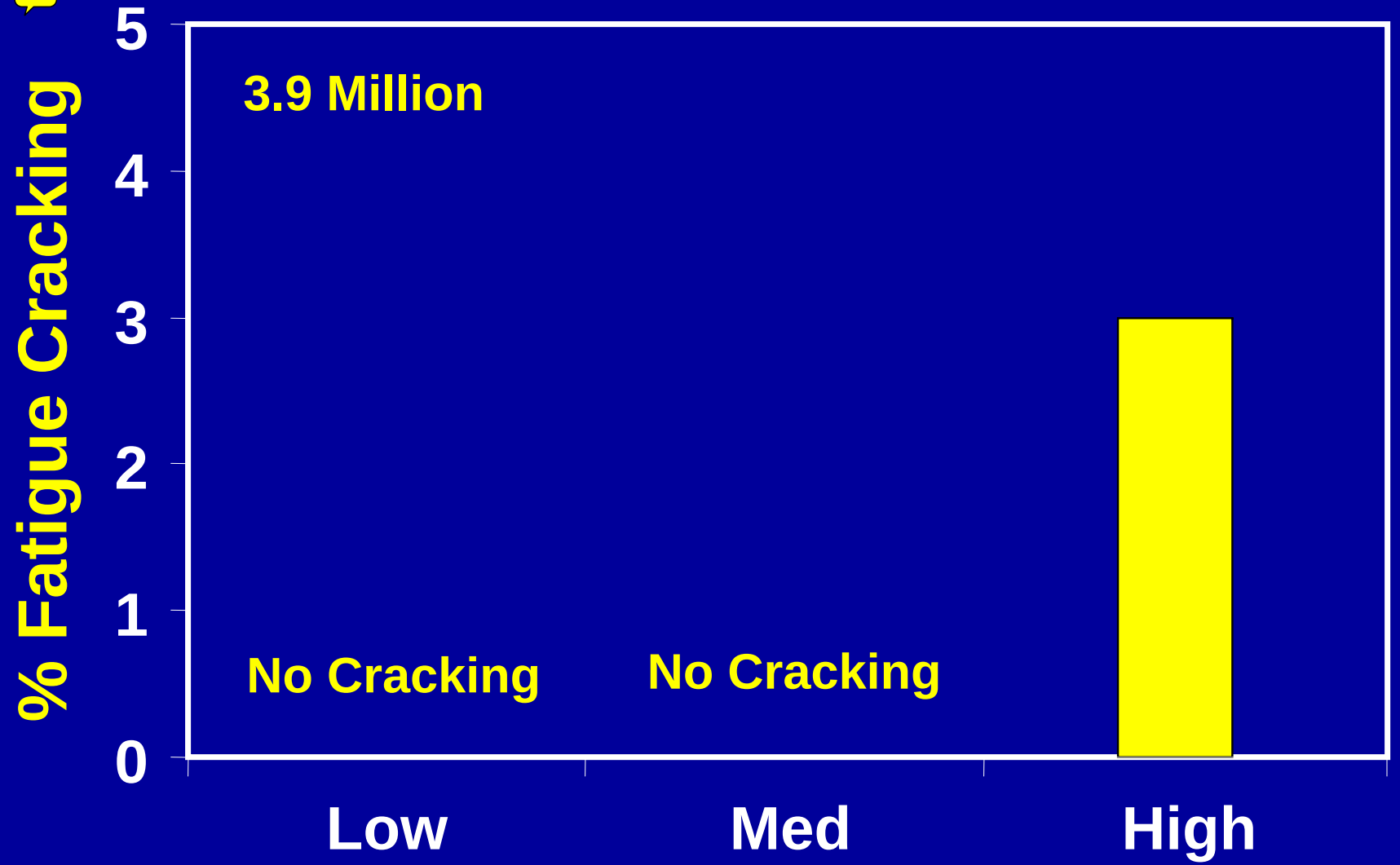
02/22/04 21:59:13 C:\DRIVE E\AR2000\RESULTS\2004\NE I-80\CYCLES TO FAILURE @ 1000 μSTRAIN=F(AIR VOIDS).spf


FEB 20 2004

Coarse at Opt. AC Content



Fine at Opt. AC Content



BUT LET'S NOT FORGET OL' WILL ROGERS

WHAT IS IT THAT WE KNOW AND WHAT IS IT THAT WE KNOW THAT AIN'T SO

WE *KNOW* THAT BITUMINOUS MIXES MADE WITH ACID IN THE ASPHALT

1. AGE FASTER (THAN ?)
2. ARE MORE SUSCEPTIBLE TO THERMAL CRACKING
3. ARE MORE SUSCEPTIBLE TO FATIGUE FAILURE
4. ARE MORE SUSCEPTIBLE TO MOISTURE (THAN ?)
5. CAN'T BE BLENDED WITH ANTI-STRIPS
6. WILL REACT DETRIMENTALLY WITH CERTAIN TYPES OF AGGREGATES

WHAT DO WE KNOW NOW?

MAYBE LESS THAN WHEN WE STARTED

1. MIXES MADE WITH ACID MODIFIED BINDERS DO SEEM TO AGE MORE RAPIDLY THAN THOSE MADE WITH POLYMER + ACID—BUT DO THEY AGE FASTER THAN UNMODIFIED BINDERS?
    1. DOES THAT MATTER IF THE LOW TEMPERATURE PROPERTIES REMAIN INTACT?
        1. STIFFER MIXES RESIST RUTTING
    2. FATIGUE IS THE QUESTION

WHAT DO WE KNOW NOW?

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

WHAT DO WE KNOW NOW?

THE ISSUE OF MOISTURE SENSITIVITY

1. THIS IS A MIX PROBLEM AND SHOULD BE TREATED AS A MIX PROBLEM
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

SOME FINAL COMMENTS

1. ACID MODIFICATION ≠ POLYMER MODIFICATION
    1. USE THE MIX ANALYSIS TOOLS WE HAVE TO DETERMINE WHERE AND WHEN POLYMER IS NEEDED
    2. ACID MODIFICATION CAN FILL A NICHE WHEN SOME ADDITIONAL BINDER STIFFNESS IS NEEDED
2. ABOVE ALL ELSE COMMUNICATION BETWEEN AGENCY, SUPPLIER AND CONTRACTOR IS ESSENTIAL TO SUCCESS

AND REMEMBER

"Errors using inadequate data are much less than those using no data at all"—Charles Babbage