PPA WORKSHOP

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MINNEAPOLIS, MN

ANALYTICAL PROCEDURES DETECTION QUANTITATIVE RECOVERY RECOVERY ISSUES

by

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SCOPE OF PRESENTATION

1. DETECTION OF PRESENCE AND AMOUNT OF PPA IN BINDERS
   a. Qualitative
   b. Quantitative
2. DETERMINATION OF PPA IN RECOVERED BINDERS
   a. Recovery procedures
   b. Problems with quantitative recovery of PPA
   c. Implications of reduced levels of PPA in recovered binder

Detection Methods

1. DETECTION--Qualitative
   a. Susan Needham at FHWA developed a qualitative method for showing the presence of phosphoric acid in asphalt
      i. Phosphoric acid is extracted from asphalt using iso or n butanol
      ii. Ammonium molybdate removes the phosphoric acid (if present) and when ascorbic acid solution is added a blue color develops indicating the presence of the acid.
      iii. Not quantitative because one can't be sure all of the phosphoric acid has been removed from the binder
      iv. Full procedure on Turner Fairbanks web site

Detection Methods

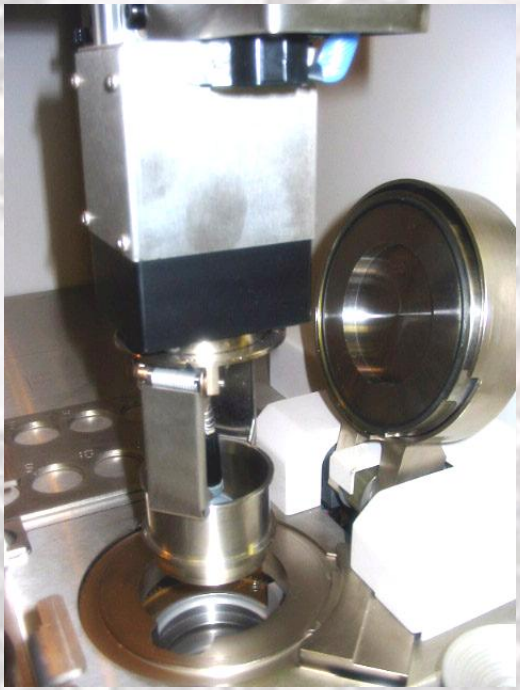
2. DETECTION--Quantitative
   a. The asphalt matrix makes direct measurement difficult
   b. ICP (Inductively Coupled Plasma) can be used but requires quantitative sample dilution
   c. MTE has developed a direct measurement procedure using Energy Dispersive X-Ray Fluorescence (EDXRF)
      i. Has the advantage that no sample prep is needed

Detection Methods

2. DETECTION—Quantitative Continued
   d. Wavelength Dispersive XRF will also perform the same test, has higher resolution, but requires more powerful X-Ray sources and is typically more costly
   e. Virgin asphalt does not contain phosphorus
   f. This technique does not directly measure phosphoric acid, it determines Phosphorus
      i. 115% PPA is 36.4% Phosphorus
      ii. %P/.364=%PPA

Instrument

- EDXRF
  - Epsilon 5 manufactured by Panalytical with a 600 W Gd-anode X-ray tube and 100kV generator.

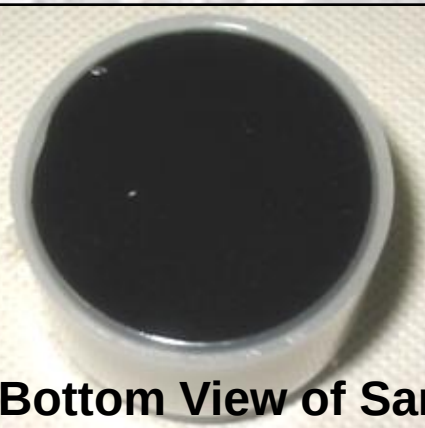


Sample Preparation

Empty Sample Holder

Filled Sample Holder

Sample in Liquid XRF Cup

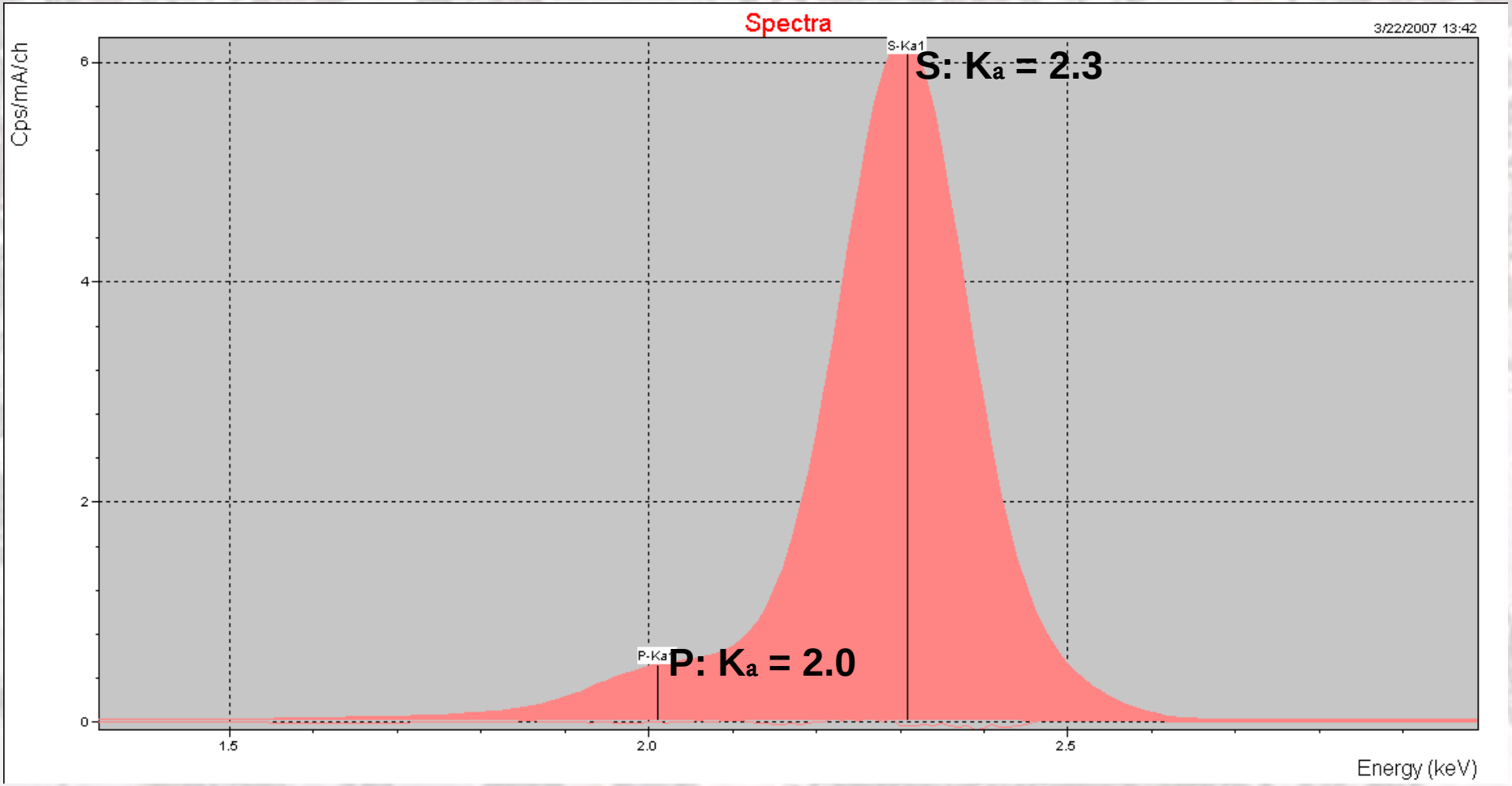


Bottom View of Sample in Liquid XRF Cup

Thanks to Olga Puzic for identifying that direct pour can work with Mylar film, although at high enough temperature it will definitely melt

Deconvolution

Because Sulfur & Phosphorus absorb in the same region there is a need to deconvolute the two signal responses



Standard ID	% P	% S
0	0.000	4.15
1	0.544	4.15
2	0.3685	4.15
3	0.284	4.15
4	0.247	4.15
5	0.116	4.15
6	0.0457	4.15
13	0.000	4.52
14	0.000	4.15
15	0.000	4.51
16	0.000	1.81
17	0.0966	1.81
18	0.266	1.81
19	0.219	1.81

Standard ID	% P	% S
20	0.000	3.434
21	0.203	3.434
22	0.322	3.434
23	0.134	3.434
24	0.000	3.369
25	0.170	3.369
26	0.353	3.369
27	0.0588	3.369
28	0.000	4.360
29	0.434	4.360
30	0.0603	4.360
31	0.156	4.360
32	0.306	4.360

Repeatability

- Plant production sample with a calculated formulation target of 0.109% P
- 4.7% higher than target

Run #	% P
1	0.113
2	0.106
3	0.119
4	0.117
Average	0.114
Std Dev	0.0057

ADDITIONAL CONFIRMATORY TEST RESULTS

- Eight samples submitted by Port Authority of New York & New Jersey
- Samples submitted blind
- Technician at Port Authority lab added differing amounts of 105% PPA to samples they received from suppliers. Two suppliers represented
- Data used with permission from PANYNJ

SAMPLE	PG GRADE used to make blend	Wt% P determined	Wt% of 105% PPA reported by MTE	Wt% Sulfur	Wt% of 105% PPA reported added by PANYNJ
A	64-22	0.012	No PPA	4.39	0
B	64-22	0.294	0.886	4.29	0.944
C	76-22+SBS	0.116	0.350	4.11	0
D	76-22+SBS	0.333	1.004	4.21	0.645
E	76-22+SBS	0.015	No PPA	4.18	0
F	76-22+SBS	0.105	0.137	4.05	0.371
G	70-22	0.016	No PPA	4.51	0
H	70-22	0.235	0.708	4.30	0.739

Comments from PANYNJ—PPA had partially solidified and some adhered to spatula, somewhat lower result expected. Sample D contained 0.35% PPA according to supplier—0.35%+0.645%=0.995%

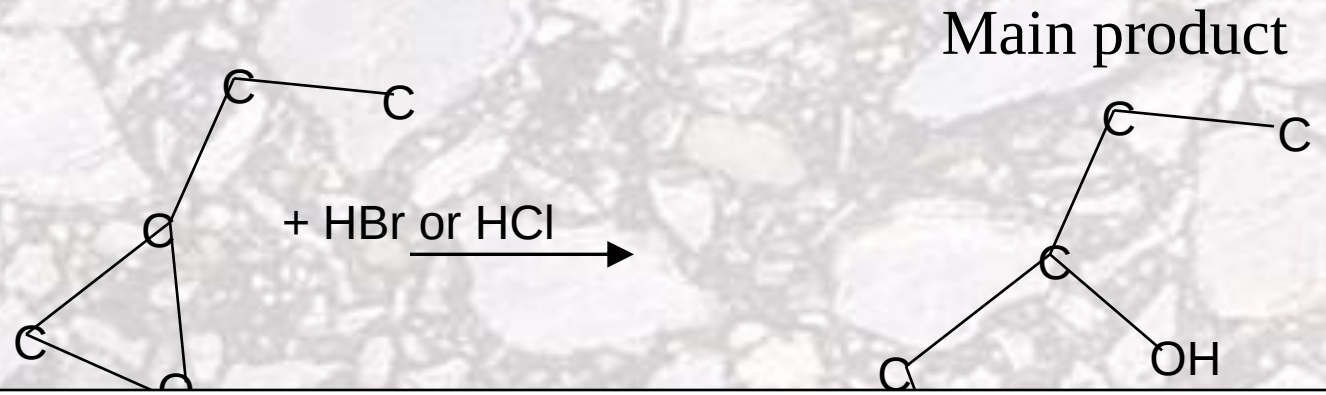
DETECTION CONCLUSIONS

1. Detection and quantification of phosphorus is possible with fairly expensive analytical equipment--$40,000 to $100,000
   a. Good calibration with a wide range of standards covering both P and S is needed if you want to obtain accurate results. If you don't adjust for S you have incorrect data
   b. Frequent checking of verification standards needed to make sure calibration hasn't drifted (e.g. weekly)
2. If you get a result showing 0.1% PPA or less chances are that is a zero. Levels that low aren't worth the expense of adding

DETERMINATION OF PPA IN RECOVERED BINDERS

1. Forensic analysis of binders extracted from mixtures for the presence of PPA is often of interest
2. There are two issues that confound extraction and recovery of binders that contain PPA
   a. Some extraction solvents neutralize acid
   b. Complete removal of phosphate from aggregate is very difficult

Both n-propyl bromide and trichloroethylene sold in commercial quantities (55 gal drums) contain 1,2 epoxy butane as a "stabilizer". In fact the stabilizer's function is to scavenge H^+ which are generated in these solvents as they age.



THE IMPLICATIONS OF THIS REACTION IN THE PRESENCE OF PPA MODIFIED BINDERS SHOULD BE OBVIOUS

BACKGROUND

Recent concerns regarding the use of PPA modified binders (PG 64-28) in New York State and in Ontario have lead to investigations which in part have included extraction and recovery of the binders from projects to determine the PG grade of the recovered binders

In many cases the PG grade of the recovered binders either did not meet PG 64 (DSR value < 1.0 kPa) and yet mechanical tests indicated similarity in performance between mixes produced with and without PPA modified binders

SOME DATA

I was ready to accept that the 64-28 could have fallen back from a PG 64 to something slightly lower than a PG 64. However, when extracting a second core taken at the same location in the travel lane the DSR value was half of the binder DSR value in the first core, I figured there had to be a cause.

SOU			
NEW YORK 2007 CORE B	64-28 (~0.8% PPA)	0.977	Reclaimed n-Propyl Bromide (nPB),
NEW YORK 2007 CORE C	64-28 (~0.8% PPA)	0.455	Virgin nPB

Project with some visible flushing was constructed in 2007 and the cores tested here were taken in October of 2007

SOME DATA

Elvaloy blend was tested by mistake, but as often happens mistakes can be useful. The results show that once the acid has

The decision was made to investigate the impact of extraction solvents on blank samples of PPA modified binders

SOURCE	BINDER TYPE	G*/SIN(DELTA) @ 64C Original	G*/SIN(DELTA) @ 64C Recovered	COMMENTS, 170 grams binder in 1 liter of solvent, Rotovap recovery
TERMINAL SAMPLE	64-28 (Elvaloy + 0.3%PPA)	1.16	1.14	Recalimed nPB
LAB SAMPLE	64-28 (0.75% PPA)	1.76	1.28	Reclaimed nPB
LAB SAMPLE	64-28 (0.75% PPA)	1.67	0.825	Virgin nPB
LAB SAMPLE	64-28 (0.75% PPA)	1.67	1.49	Toluene

After evaluating the asphalt blanks, we went back to New York

NEW YORK 2007 CORE 12C	64-28 (~0.8% PPA)	0.455	Virgin nPB
NEW YORK 2007 CORE 12A	64-28 (~0.8% PPA)	1.93	Toluene
NEW YORK 2007 CORE 3C	64-28 (~0.8% PPA)	2.66	Toluene
NEW YORK 2007 CORE 15C	64-28 (~0.8% PPA)	1.15	Toluene
NEW YORK 2007 CORE 15B	64-28 (~0.8% PPA)	2.32	Toluene
NEW YORK 2007 CORE 15A	64-28 (~0.8% PPA)	1.96	Toluene

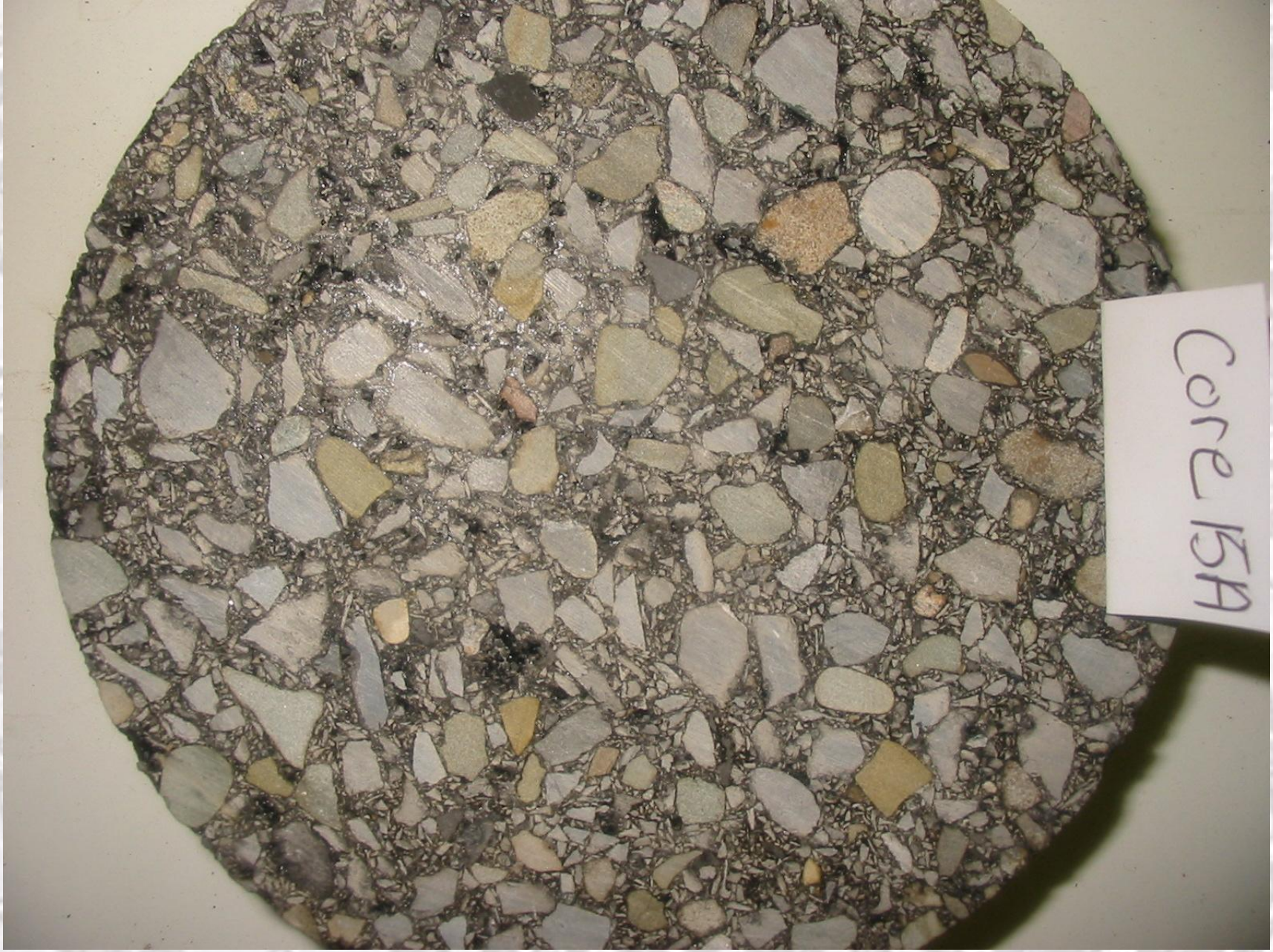
PICTURES OF CORES FROM NEW YORK THAT WERE EXTRACTED

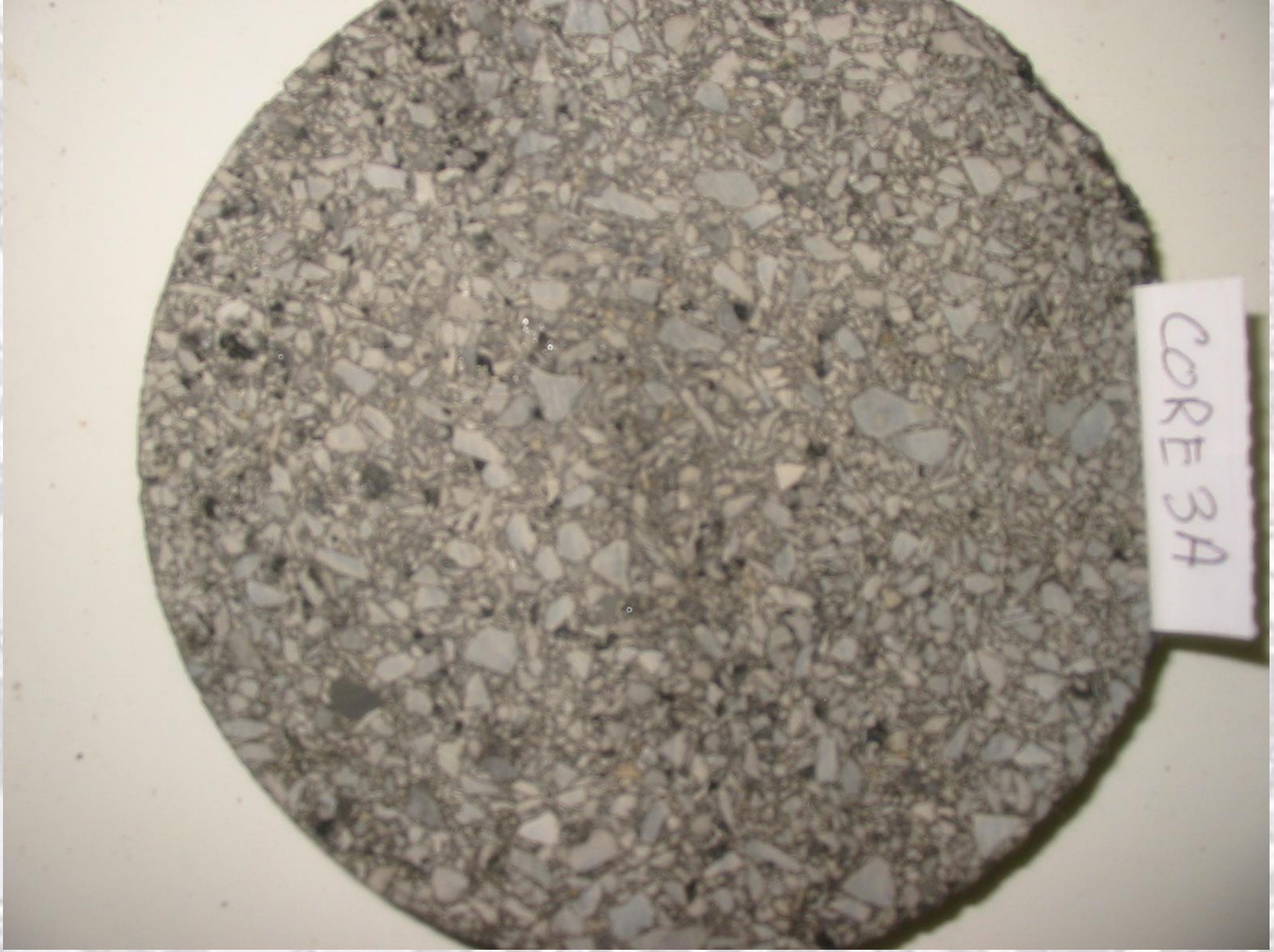
1. The pictures that follow were taken on the bottom of the top lift after the top lift was sawed away from the complete core
2. Since these are literally "snapshots" of the project they don't provide proof of a cause to the flushing issue in New York
3. However given that the recovered binders don't show a degradation of PG grade the core surfaces suggest alternate avenues for investigation


Core 12A


Core 12B


Core 15B


Core 15A


CORE 3A


Core 3C

DATA from Ontario cores

SOURCE, Mix in Place 3 years	BINDER TYPE	G*/SIN(DELTA) @ 64C Recovered	Low temp PG grade of recovered binder (PAV)	COMMENTS, Centrifuge Extractor, Rotovap recovery
Ontario Core location 3	64-28 (PPA Level unknown	0.742	-36.3°C	nPB
Ontario Core location 3	64-28 (PPA Level unknown	1.27 Ratio=1.71	Not tested but same location as previous	Toluene
Ontario Core location 3, new station	64-28 (PPA Level unknown	1.64	-31.6°C	nPB
Ontario Core location 3, new station	64-28 (PPA Level unknown	2.98	no test	nPB Soxhlet, top 1/2 inch of core
Ontario Core location 2	64-28 (PPA Level unknown	1.24	-34.6°C	nPB
Ontario Core location 2, portion of core from previous test	64-28 (PPA Level unknown	2.16 Ratio = 1.74	No test	toluene
Ontario Core location 2, new station	64-28 (PPA Level unknown	1.99	-30.3°C	nPB
Ontario Core location 2, new station	64-28 (PPA Level unknown	2.49	no test	nPB Soxhlet, top 1/2 inch of core

MNRoad DATA

SOURCE	BINDER TYPE	G*/SIN(DELTA) @ 58C Recovered	COMMENTS, Centrifuge Extractor, Rotovap recovery
HMA PLANT MIX	58-34 (0.8% PPA)	21.3	Toluene
HMA PLANT MIX	58-34 (0.8% PPA)	13	Virgin nPB

CONCLUSIONS REGARDING SOLVENT ISSUES

1. USE A SOLVENT THAT IS KNOW TO NOT CONTAIN AN ACID SCAVENGER
   a. Reagent grade trichlorethylene or n-propyl bromide
   b. Toluene
   c. THF

   BE SURE TO EXERCISE CARE WITH ALL SOLVENTS ESPECIALLY THOSE THAT ARE FLAMMABLE

RECOVERY OF PHOSPHORUS FROM MIXTURES

1. THERE IS A DESIRE AT TIMES TO QUANTITATIVELY DETERMINE THE AMOUNT OF PPA IN MIX
2. DON'T CONFUSE THE AMOUNT OF PHOSPHORUS RECOVERED WITH THE DEGREE OF ACID REACTION WITH THE BINDER
   a. The H^+ ion reacts with the binder not the PO_4^{-3} group, HPO_4^{-2}, or $H_2PO_4^{-1}$ group
   b. Reduction of P in the recovered binder does not necessarily mean a loss of binder stiffness

EXTRACTION OF PPA MODIFIED BINDER FROM MIXES

- Sample prepared at a calculated 0.746% of 115% PPA (0.746*0.3631= 0.271% P
- EDXRF result—0.269% P or 0.741% PPA
- MIX TESTING TO BE PERFORMED
  - Use granite, siliceous gravel, limestone aggregates. Mix 6% binder with material finer than 4.76 mm sieve, condition overnight at 100°C
  - Extract, recover the binder. Test for %P in binder

% Phosphorus in Binder Recovered from mix

0.269% P in original binder	Cisler/granite	Wimmie/siliceous gravel	Waldenberger/limestone
% Phosphorus in 64-28 binder as determined by EDXRF	0.269%	0.269%	0.269%
n-Propyl Bromide #1	0.103%	0.211%	0.149%
n-Propyl Bromide #2	0.073%	0.160%	0.177%
85% Toluene & 15% Ethanol	0.029%	0.151%	0.017%

% Phosphorus Recovered by Extraction

	Cisler/granite	Wimmie/siliceous gravel	Waldenberger/limestone
% Phosphorus in 64-28 binder as determined by EDXRF	0.269%	0.269%	0.269%
n-Propyl Bromide #1	38.3%	78.4%	55.4%
n-Propyl Bromide #1	27.1%	59.5%	65.8%
85% Toluene & 15% Ethanol	10.8%	56.1%	6.3%

These data show that at least for these mixes lack of Phosphorus recovered in the binder does not equate to loss of stiffness in the recovered binder

Binder contained 0.269% P,	after 1 extraction	er after 2 extractions
		1.32 kPa @ 64°C
THF Extracted granite agg	0.088% P equals 32.7% recovery	0.122% P Equals 45.3% recovery
		1.88 kPa @ 64°C
THF extracted limestone agg	0.102% P equals 37.9% recovery	
		1.77 kPa @ 64°C

Appears as though THF is no more effective as a primary extraction solvent than n-Propyl Bromide

IMPACT OF NEUTRALIZATION ON PHOSPHORUS LEVEL

1. SAMPLE PPA MODIFIED BINDER, 64-22 + 0.75% PPA YIELDING A PG 70-22 WAS TREATED WITH 0.7% ADHERE AMINE ANTISTRIP. PHOSPHORUS CONTENT AND BINDER STIFFNESS TESTED

	% P BY XRF	% Acid, CALCULATED	
81A Flnt Hlls, PPA, Neat	0.291	0.8	
002A 81A w/ 0.7% Adhere	0.286	0.79	
	G*/Sin delta	G*/Sin delta	
	@64°	@70°	
81A Flint Hlls, PPA, Neat	3.01	1.49	
002A 81A w/ 0.7% Adhere	1.5	0.74	

PRESENCE OR LACK OF PHOSPHORUS IS NOT AN INDICATOR OF ACID MODIFICATION IS PRESENT AND FUNCTIONING

CONCLUSIONS OF EXTRACTION & RECOVERY TESTING

1. REGARDLESS OF AGGREGATE TYPE IT IS IMPOSSIBLE TO QUANTITATIVLY RECOVER ALL OF THE PHOSPHORUS ADDED TO MIX WITH THE SOLVENTS WE HAVE INVESTIGATED
   a. n-PROPYL BROMIDE, TOLUENE, THF
   b. We may look at CS_2, but only for research completeness—not practical on a regular basis

CONCLUSIONS OF EXTRACTION & RECOVERY TESTING

2. From several investigations it appears as though the extraction & recovery process does not show a (substantial) loss of binder stiffness.
3. This last point is difficult to prove since we have no way of knowing precisely what the binder stiffness in the mix actually is.
   a. Issues of mix aging based on curing time & temp
   b. Clearly if we obtain DSR values < the original binder we know we have a problem

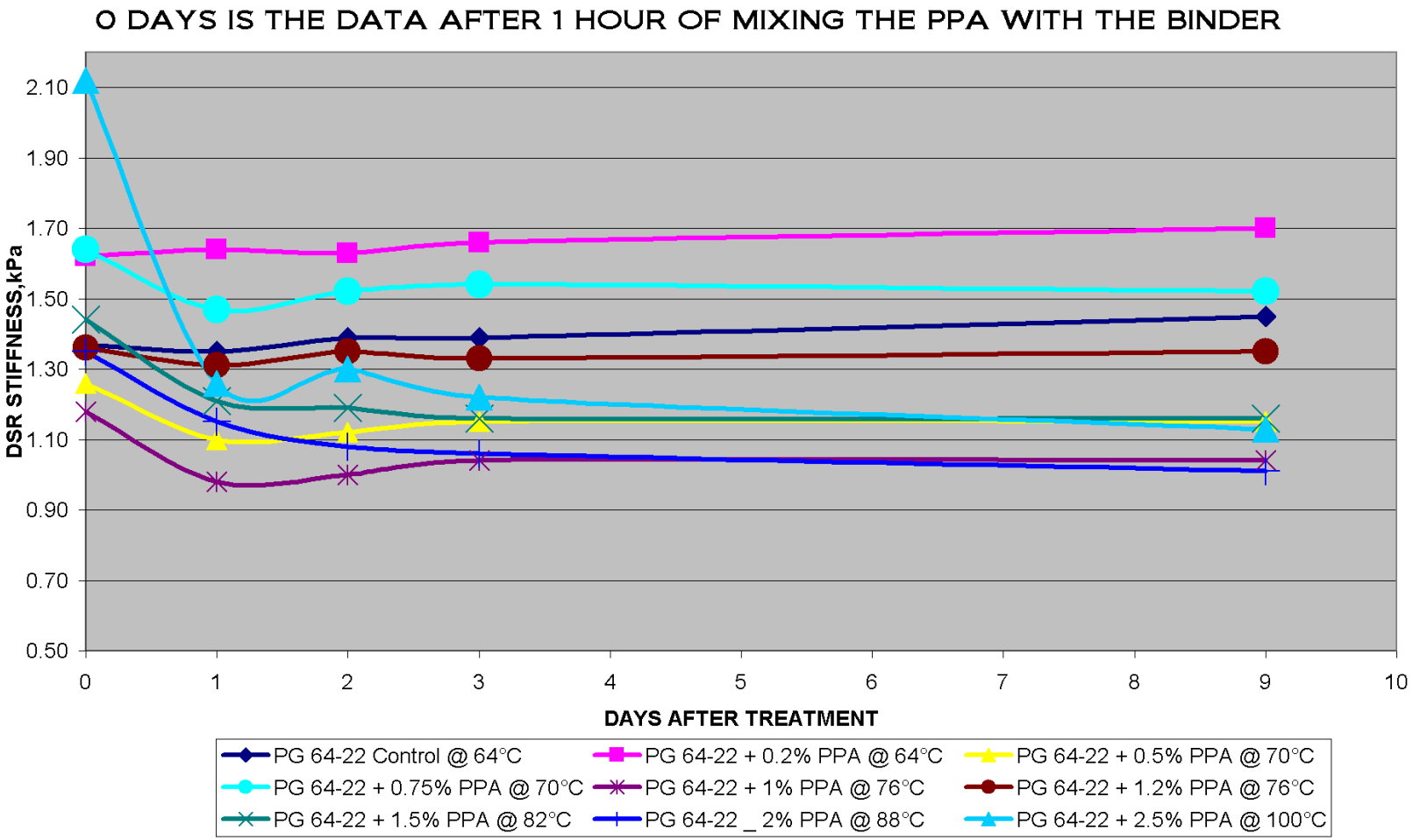
TIME TRACK STUDY

1. PURPOSE—ASCERTAIN THE STABILITY OF BLENDS OF BINDER WITH DIFFERING LEVELS OF PPA
2. DESIGN
   a. Track blends of PG 64-22 with increasing amounts of PPA over several days
   b. 0, 1,2,3 and 9 days (after 3 days samples were left at room temperature for 5 days before reheating and testing
   c. PPA levels = 0%, 0.2%, 0.5%, 0.75%, 1.0%, 1.2%, 1.5%, 2.0%,2.5%, 3.0%

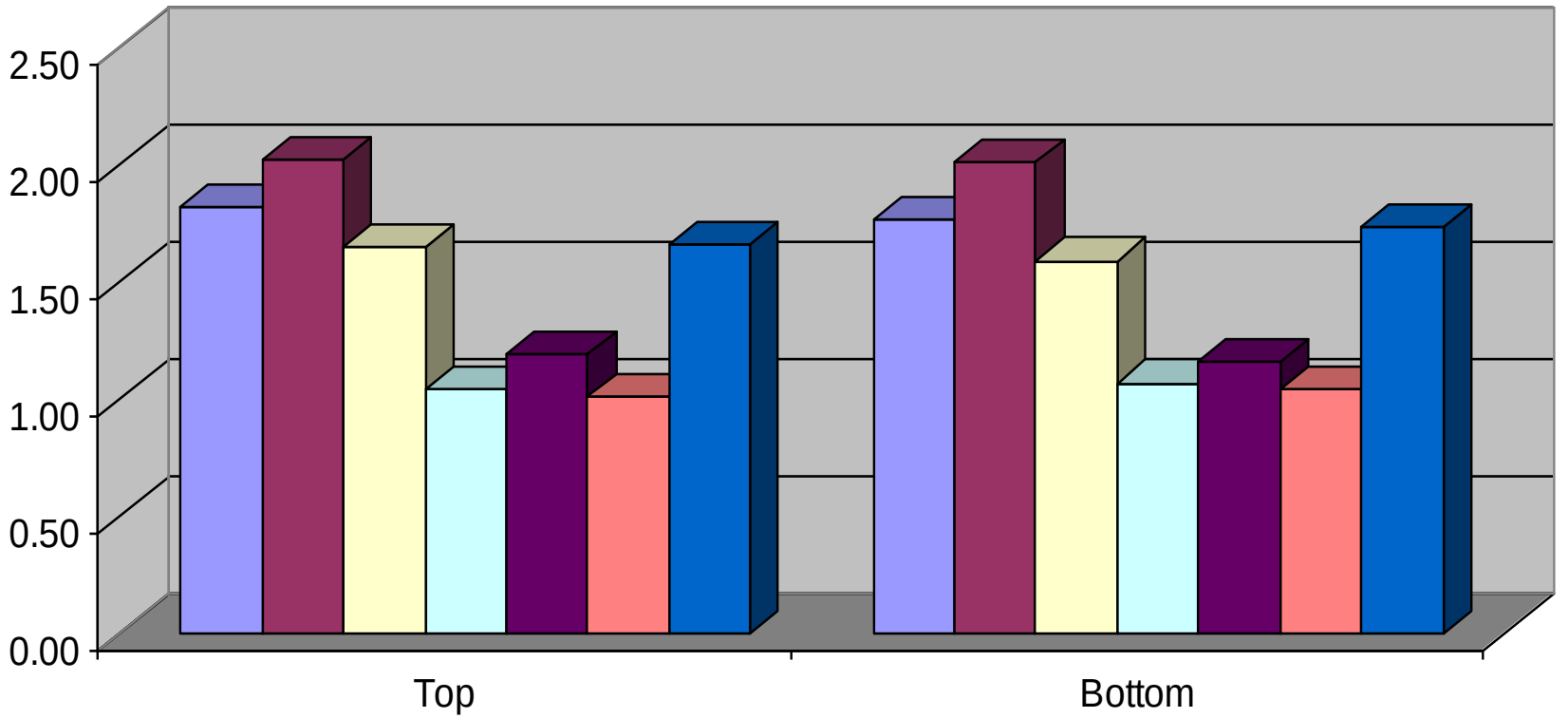
TIME TRACK STUDY—cont'd

d. After reheating on 9th day cigar tube separation tests were poured and samples allowed condition at 165°C for 4 days
e. Tubes removed, cooled and top and bottom halves tested for DSR and % PPA

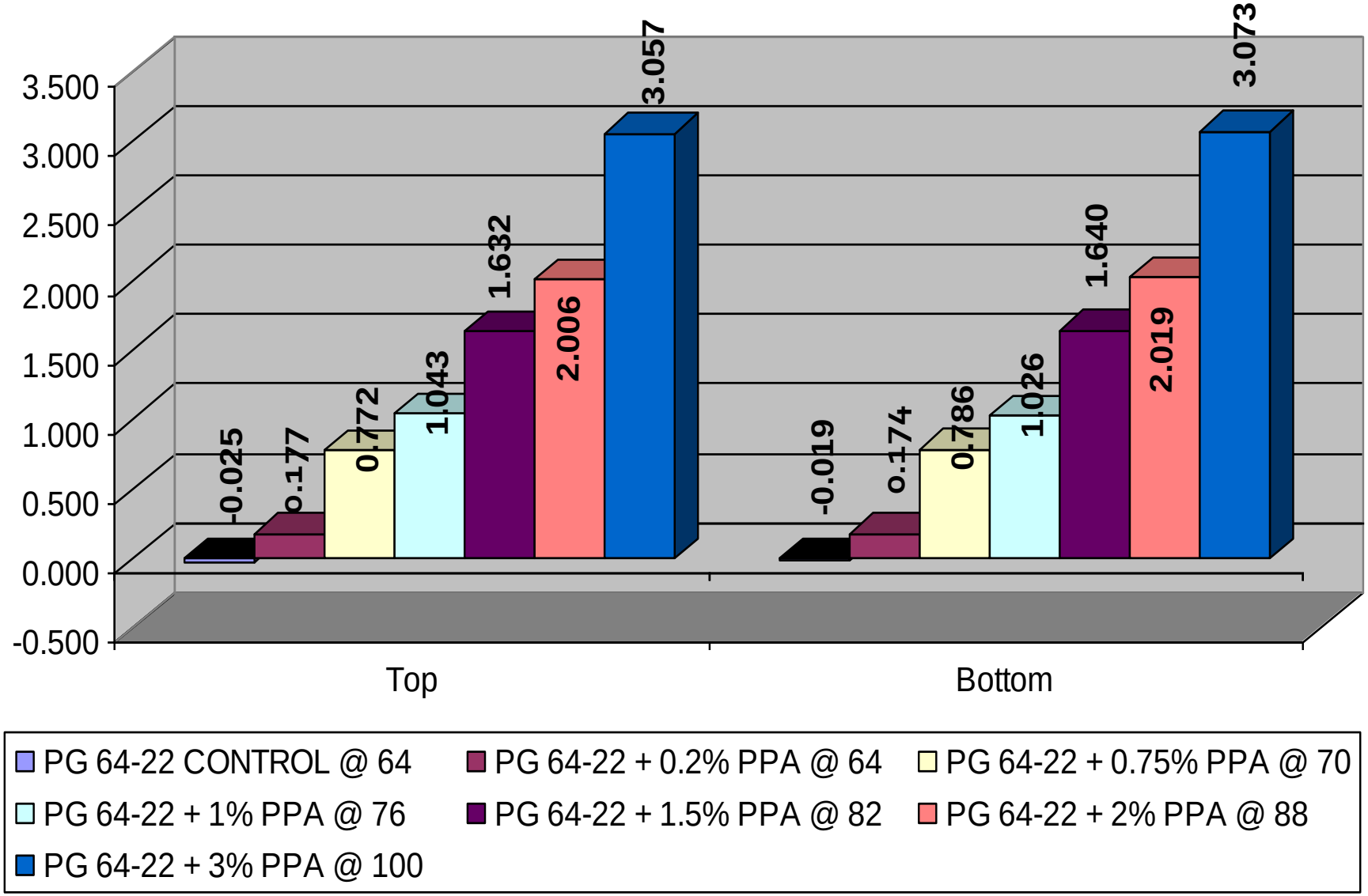
TIME TRACK STUDY OF BINDER MODIFIED WITH INCREASING LEVELS OF PPA



COMPARE DSR STIFFNESS OF TOP AND BOTTOM AFTER 4 DAY SEPARATION TEST



COMPARE % PPA IN TOP AND BOTTOM AFTER 4 DAY SEPARATION TEST



CONCLUSIONS OF TIME TRACK & CONCENTRATION STUDY

1. FOR FLINT HILLS 64-22 IT APPEARS AS THOUGH PPA LEVELS AS HIGH AS 1.2% ARE STABLE OVER THE TIME PERIOD INVESTIGATED. 1.5% APPEARS TO SHOW SOME MINOR LOSS OF STIFFNESS OVER TIME
2. FOR ALL LEVELS OF PPA THERE DOES NOT APPEAR TO BE A SEPARATION PROBLEM BASED ON EITHER DSR OR % PPA AFTER 4 DAYS OF 165°C STATIC SEPARATION CONDITIONING

FINAL THOUGHTS

1. SUCCESSFUL PAVEMENT CONSTRUCTION IS A COOPERATIVE EFFORT BETWEEN AGENCY(DESIGNER), CONTRACTOR AND SUPPLIER
2. IT IS INCUMBENT UPON ALL OF US TO PROVIDE THE BEST RESEARCH, PRODUCTS AND WORKMANSHIP OF WHICH WE ARE CAPABLE—BECAUSE WE ARE ALL CONSUMING THE PUBLIC'S MONEY

THANK YOU FOR YOUR ATTENTION

QUESTIONS

COMMENTS

SCOPE

1. DETECTION