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Pilot Study of Cellulose Nanocrystal (CNC) Use in Bituminous Materials

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16. Abstract

This report's primary objective was to assess cellulose nanocrystals (CNCs) within bituminous mixtures. Brittleness potential as measured by Cantabro Mass Loss testing was the primary evaluation mechanism. This work did not investigate economic or logistical/production factors, but rather focused on pilot level evaluations relative to the potential of CNC's to improve brittleness tendencies of bituminous mixtures. Dense graded asphalt produced with a few different combinations at 163 ºC temperatures were evaluated in conjunction with freeze dried CNC's. The overall assessment for freeze dried CNC's in dense graded asphalt was they performed in a manner comparable to, perhaps slightly worse than, control mixtures without additives. Sand asphalt produced with emulsions and aqueous CNCs at 65 ºC was also evaluated. At some dosage rates, a drastic behavior improvement was observed across a range of treatments ranging from unaged, to combined effects laboratory conditioning, to field aging. Aqueous CNCs used in conjunction with asphalt emulsion to produce mixtures at temperatures on the order of 65 ºC had technical merit and it is recommended for a more comprehensive investigation to be performed in this regard.

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LIST OF SYMBOLS AND ACRONYMS

1F	1 year of field aging at CPL
2F	2 years of field aging at CPL
AASHTO	American Association of State Highway and Transportation Officials
Abs.	percent water absorption
AC	asphalt cement
AC('14)	PG 67-22 asphalt cement source provided in March, 2014
AC('17)	PG 67-22 asphalt cement source provided in May, 2017
ANOVA	analysis of variance
Avg	average value
AQ	aqueous
B	blend of aggregates
BHD	baghouse dust
CG	1/2" crushed gravel (1 or 2)
CML	Cantabro Mass Loss
CMRC	Construction Materials Research Center
CNC	cellulose nanocrystal
CP	conditioning protocol
CPL	Columbus parking lot
CP7	Conditioning Protocol 7 – oven, hot water, and FT effects
CRS	cationic and rapid setting
CTO	crude tall oil
DGA	dense graded asphalt

DMSO	dimethyl sulfoxide
FD	freeze-dried
FPL	Forest Products Laboratory
FT	freeze-thaw
G_{mb}	mixture bulk specific gravity
G_{mm}	mixture maximum specific gravity
G_{sa}	aggregate apparent specific gravity
G_{sb}	aggregate bulk specific gravity
HCl	hydrogen chloride
HL	hydrated lime
LA	Los Angeles
$LS_{1/4}$	1/4×0 limestone
LS_{89}	No. 89 limestone
M	mix
Max	maximum value
MDF	medium density fiberboard
Min	minimum value
ML	mass loss
MS	Mississippi
MSU	Mississippi State University
n	number of mixtures evaluated within a group
N_{des}	design number of gyrations
N_{gyr}	number of SGC gyrations

No.	number
NMAS	nominal maximum aggregate size
P_b	total binder content of a mixture
$P_{b(AC)}$	portion of a mixture's total binder content provided by asphalt cement
$P_{b(EM)}$	portion of a mixture's total binder content provided by emulsion
$P_{b(RAP)}$	portion of a mixture's total binder content provided by RAP
$P_{b(RAS)}$	portion of a mixture's total binder content provided by RAS
PG	performance grade
PPA	polyphosphoric acid
RAP	reclaimed asphalt pavement
RAS	recycled asphalt shingles
S	sand (1 or 2)
SA	sand asphalt
SGC	Superpave Gyratory Compactor
Stdev	standard deviation
STOA	short-term oven aging
TGA	thermogravimetric analysis
T_{Prod}	mixing temperature
USDA	United States Department of Agriculture
V_a	air voids

CHAPTER 1-INTRODUCTION

1.1 General and Background Information

Cellulose nanocrystals (CNCs) are an emerging material with considerable possibility for many applications, construction materials being one application. CNC use in concrete (e.g. Cao et al. 2015) has shown promise. For example. Fu et al. (2017) reported CNCs improving degree of hydration in cement pastes and improvement of flexural strength by up to 20%. Given the potential of CNCs in concrete, this report is a pilot evaluation to evaluate their potential in bituminous materials as applications in this arena are not easily identifiable.

There are several potentially useful products that can be made from plants. Cellulose is the most abundant natural polymer available on Earth with its main sources being wood pulp and cotton fibers. Li et al. (2017) estimated cellulose and its derivatives as the most abundant renewable organic materials in the biosphere with annual production estimated to be over $7.5(10^{10})$ tons. Cellulose often is present in plant cell walls where it provides structure. Cellulose can also be found in marine animals, bacteria, fungi, and algae. Bulk cellulose consists of two regions (highly ordered crystalline regions and amorphous regions) that vary in proportion based on its source. When subjected to treatment, the highly crystalline regions can be extracted to result in the formation of CNCs (George and Sabapathi 2015). Generally, nano-scale cellulose fibers are referred to as nanocellulose. They are derived from cellulose and have at least one dimension in the nanometer (nm) range. Representative diameters are 5 to 70 nm and representative lengths are 100nm to several micrometers (Brinchi et al. 2013).

Current applications of CNCs include products such as pH sensors, Pickering emulsions (i.e. emulsions that are stabilized by solid particles), and reinforcing agents for polymer nanocomposites (George and Sabapathi 2015). Challenges that have limited industrial use include prediction of long-term properties and issues with water sorption as well as concerns with thermal stability, durability, and safety (Brinchi et al. 2013). CNC's can bio-degrade under appropriate environmental conditions.

1.2 Objectives and Scope

The objective of this report is to assess CNCs within bituminous mixtures. Generally speaking, two families of bituminous mixtures were evaluated: 1) dense graded asphalt (DGA) and sand asphalt (SA). Two forms of bituminous asphalt materials were evaluated: 1) performance graded (PG) asphalt binders that are customarily used at high temperatures within plant mixed asphalt; and 2) emulsified asphalt binders that are used at much lower temperatures in several different manners.

These assessments were performed primarily with respect to brittleness potential by measuring mechanical properties of compacted mixtures that were unconditioned (i.e. virgin), laboratory conditioned to simulate field aging, and field aged outdoors over time. The field aging occurred at a controlled site that has been used for dozens of mixtures over a several year period by the Construction Materials Research Center (CMRC) at Mississippi State University (MSU). Cracking and brittleness potential are one of the most formidable challenges being faced by the modern asphalt paving industry (e.g. Howard et al. 2016), and as a result, emphasis was placed on reducing brittleness potential of mixed and compacted bituminous materials.

1.3 Abbreviated Literature Review

CNCs can be dispersed in a variety of materials including water, dimethyl sulfoxide (DMSO), and acids such as hydrogen chloride (HCl). Acid hydrolysis seems to be the most common extraction mechanism from biomass in present day (Brinchi et al., 2013), with HCl generally resulting in higher thermal degradation temperatures. Following acid hydrolysis, CNCs are often diluted with water and then dialysis against the water is performed to remove free acid and sugar molecules (Habibi et al. 2010). CNC particles are isolated from water in numerous ways including air-drying, freeze-drying, or spray-drying. Each drying method produces a different CNC product. When left undisturbed to air-dry, the resulting CNCs form a solid but brittle film that is glossy and iridescent. Freeze-dried CNCs usually result in a product made up of thin lamellar flakes while spray-dried CNCs typically result in a free-flowing and flour-like powder (Beck et al. 2012). Regardless of drying procedure, dry CNCs have a very high surface-to-volume ratio.

Rheological behavior of CNCs is highly dependent on concentration. At high concentrations they exhibit an elastic gel-like behavior while at low concentrations they exhibit viscous liquid like behavior. (Li et al. 2015). The theoretical tensile strength of CNCs is roughly 7.6 GPa, while their elastic modulus is approximately 150 GPa (George and Sabapathi 2015). Also reported by George and Sabapathi (2015), CNCs show shear thinning behavior at lower concentrations. Generally speaking, and not referring to any specific application, CNCs have the potential to fill a size gap between the molecular level and the fibrous level. They have high aspect ratios, high mechanical properties, low thermal expansion, low density, and surface-accessible hydroxyl groups that can readily be chemically modified to give additional functionalities (Moon et al. 2016).

Temperature susceptibility is an obstacle to overcome for many bituminous applications. Molnes et al. (2016) reviewed several works and reported that CNCs break down above 220 ºC; experiments were performed on dried CNCs with an inert atmosphere of nitrogen gas. Interactions with CNC experts at the United States Department of Agriculture (USDA) Forest Products Lab (FPL) revealed the following. High lignin CNCs, as of the 2018 time frame, were indicating a degradation temperature (short duration) in thermogravimetric analysis (TGA) of roughly 300 ºC. For extended durations, this temperature was expected to decrease in the view of USDA-FPL experts. CNCs were noted to thermally degrade above around 160 ºC (320 ºF), but coating in ethylene glycol might be helpful for reducing temperature susceptibility.

CHAPTER 2 – EXPERIMENTAL PROGRAM

2.1 Overview of Experimental Program

Two families of mixes were evaluated in this report: dense graded asphalt (DGA) and sand asphalt (SA). DGA is a mixture with a gradation that might be used by an agency such as a DOT to conform to American Association of State Highway and Transportation Officials (AASHTO) M323. SA is a mixture where almost all particles pass a No. 4 sieve. Twelve DGA mixes and three SA mixes were evaluated. These fifteen mixes were given mixture ID's that align with a multi-year aging experiment performed in Columbus, MS at a location known as the Columbus Parking Lot (CPL). The twelve DGA mixtures were Mix 23 (M23), M35, M37, M38, and M39 to 46. The three SA mixes were given ID's of M47 to M49. Generally speaking, mixes have been numbered in an ascending order as produced for cases where at least some of the replicate specimens produced were placed onto the CPL.

Within these fifteen mixes, there are two DGA mix families and one SA family. M23, M35, M37, and M38 were patterned after a mixture that is produced as a paving material by APAC-Mississippi, Inc. M39 to M46 were produced with all gravel aggregates to reduce variables in a more controlled DGA data set. M47 to M49 were SA that used lower temperatures and emulsified asphalts. DGAs used higher temperatures and PG binders. There is a companion effort to this report that was also performed for USDA-FPL where bio-rejuvenators were evaluated. Mixes M21 to M36 were produced for the bio-rejuvenators effort, where M23 and M35 served dual use in the CNC and bio-rejuvenators evaluations.

A total of 168 bituminous specimens were compacted and tested for mechanical properties in this experimental program. A few additional specimens were also produced and used as part of initial investigations that are discussed in this chapter to the extent that is relevant to understanding this work and its outcomes. Of these 168 specimens, 150 were produced specifically for this report; 18 specimens (9 each from M23 and M35) were also used in the bio-rejuvenators companion work for USDA-FPL.

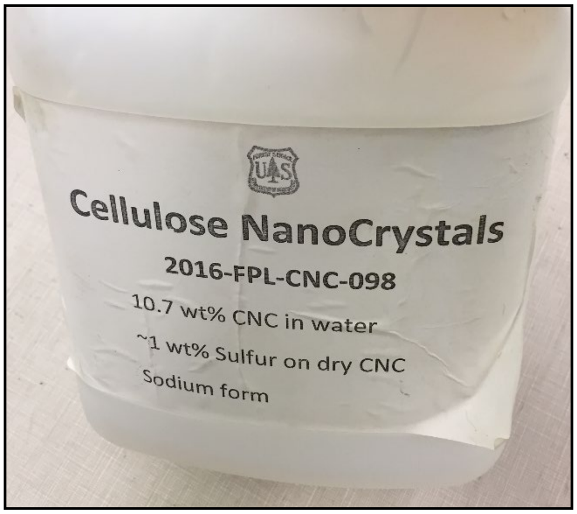
2.2 Materials Tested

2.2.1 Cellulose Nanocrystals (CNCs)

Two CNCs were supplied to MSU by USDA-FPL for evaluation (Figure 2.1). Water dispersed and freeze-dried CNCs were evaluated in this report, but in different manners. Water dispersed (gel) CNCs were evaluated at lower temperatures in conjunction with emulsified asphalt, while freeze-dried (powder) CNCs were evaluated at traditional hot mixed asphalt temperatures.

CNCs were provided in a gel (aqueous, or AQ) form. In this case, CNCs were suspended in water at 10.7% by weight. This product was an opaque viscous liquid with a bulk density of roughly 1 g/cm^3, a neutral pH, and 1% by weight sulfur residual on dry CNC in sodium form. The gel product is referred to hereafter as AQ-CNC, or just AQ in some instances. The AQ-CNC was sampled from batch 2016-FPL-CNF-098.

High lignin CNC was also supplied by USDA-FPL in a freeze-dried cake. This product is referred to hereafter as FD-HL-CNC, or just FD in some instances. The material was extracted from 40 mesh (400 µm) poplar wood chips as described in Agarwal et al. (2018). These CNCs have 1% by weight sulfur residual on the dry CNC in sodium form. In its solid, freeze-dried state it is dark brown in color and can be broken apart into a fine powder for use. FD-HL-CNC was stated by USDA-FPL to be, relatively speaking, thermally stable. The FD-HL-CNC was sampled from batch 2017-FPL-CNC-112, and the label of the sample obtained stated the material was extracted from Yreka medium density fiberboard (MDF) at 185 ºC for 180 minutes.



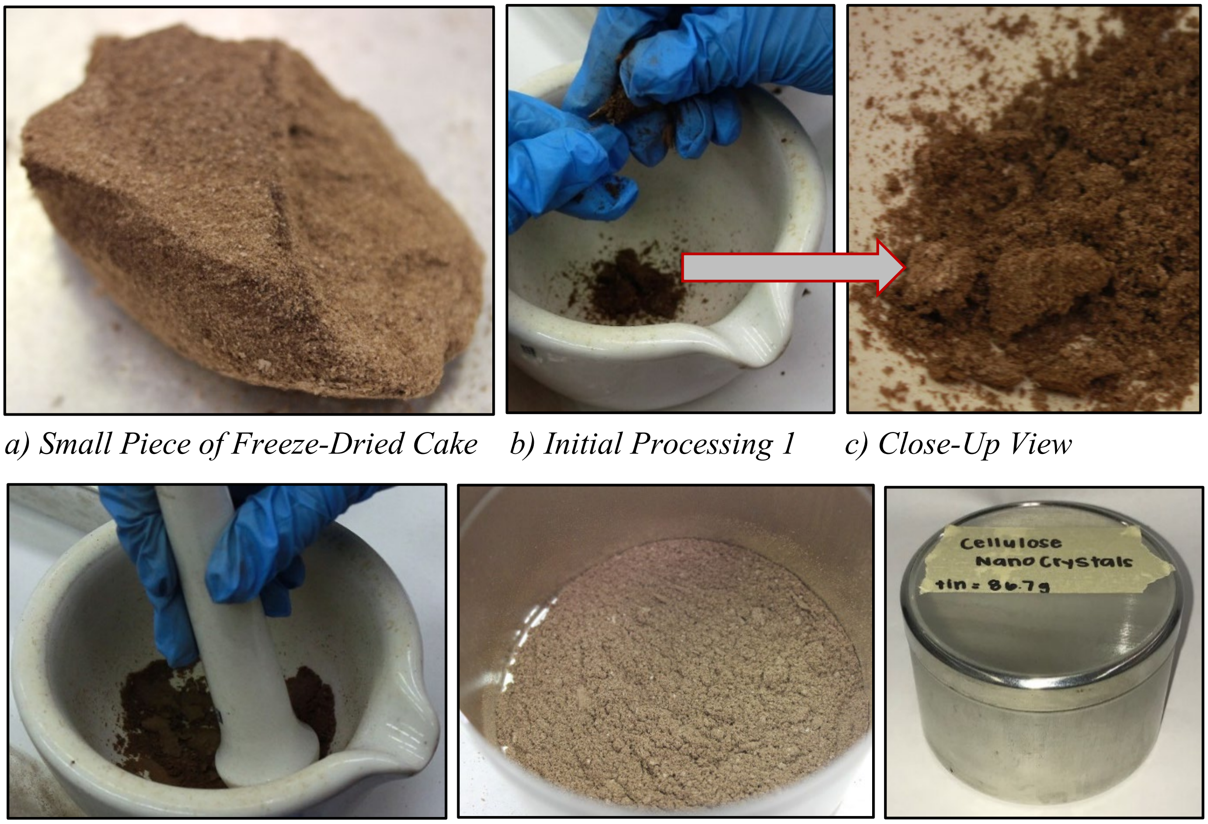
a) CNC Gel (CNC_G)

b) CNC Powder (CNC_S)

Figure 2.1. Photos of CNC Materials As Supplied by USDA-FPL

CNC materials were handled in accordance with USDA-FPL guidance. AQ-CNC was stored in a cabinet at room temperature, and prior to use, the container was agitated manually with a plastic stirrer, and once stirred for a few seconds, samples of the material were batched for use.

The following steps were utilized to process the FD cake of CNC prior to blending into bituminous material. Processing occurred with ample ventilation while the operator wore an N100 mask, latex gloves, and goggles. First, a small portion (roughly 2 g) of the freeze-dried cake was broken off by hand (Figure 2.2a). Next, this piece was broken down by rubbing between fingers into a ceramic dish (Figure 2.2b and 2.2c). After hand processing, a mortar and pestle was used to further process the material to a point of visually consistent fineness (Figure 2.2d). Thereafter, the material was transferred to metal tins for storage in a cabinet in air conditioning (Figures 2.2e and 2.2f). Several iterations of the aforementioned process were performed to fill one metal tin.



a) Small Piece of Freeze-Dried Cake *b) Initial Processing 1* *c) Close-Up View*

d) Mortar-Pestle Processing *e) Processed Material* *f) Storage*

Figure 2.2. Processing FD-HL-CNC

2.2.2 Bio-Rejuvenators

Crude Tall Oil (CTO) was supplied by Ingevity from Deridder, LA. CTO is an acidulated product from sulfate black liquor skimmings containing straight chain C_{18} and cyclic C_{20} organic acids. At 25°C, CTO is a liquid with a specific gravity of roughly 0.97 g/cm^3. CTO is a dark color (i.e. amber to dark brown), with a melting point of roughly -20°C and a boiling point of roughly 346°C. Cleveland open cup flash point is roughly 200°C. CTO is chemically stable, and has a dynamic viscosity at room temperature of 200 to 800 cP. One sample of CTO was obtained that was used for all work in this report and also for all work in the corresponding bio-rejuvenators work.

2.2.3 Bituminous Materials

Two performance graded (PG) asphalt binder samples and one emulsified asphalt were used in this report, all of which were supplied by Ergon, Inc. Both PG products graded as 67-22, and neither contained any additives such as polyphosphoric acid (PPA) or polymers. Generally speaking, asphalt cement (AC) is a term often used for bituminous materials that are absent acids, polymers, or other additives and asphalt binder is a term used for a product that is graded and sold in the marketplace that may or may not contain bituminous modifiers. AC is a slightly more specific term than asphalt binder, but for the two PG 67-22 products used in this report, they can be used interchangeably.

Both PG 67-22 products came from Ergon's Vicksburg, MS refinery. Mixes M23, M35, M37, and M38 were produced with a single sample labeled AC('17) since the material was sampled in May of 2017. For reference, all mixes produced from M21 through M38 for this report and the companion bio-rejuvenators report were produced with the large AC('17) sample. These mixes depleted this sample, and to produce mixes M39 to M46, an existing sample of PG 67-22 from Ergon's Vicksburg, MS refinery was available at CMRC. This sample was taken in March of 2014, was labeled AC('14), had comparable properties to AC('17), and as such was used to produce mixes M39 to M46. Other than for transparency, there is little reason further differentiate AC('14) and AC('17) for purposes of this project.

One asphalt emulsion graded CRS-2P was sampled and supplied in May of 2019 by Ergon in individual 1-gallon plastic jugs. This CRS-2P source had a 68% asphalt residue. This emulsion sample was used to produce mixes M47 to M49.

2.2.4 Virgin Aggregates and Fillers

Six virgin aggregates and two fillers were used in this report. The two fillers (particles mostly passing a 0.075 mm sieve) were hydrated lime (HL) and baghouse dust (BHD), both of which were obtained from APAC's facility in Meridian, MS. Table 2.1 summarizes typical properties of these virgin aggregates. Four of these virgin aggregates were used to produce mixes M23, M35, M37, and M38. They are: No. 89 limestone (LS_{89}), 1/4×0 limestone ($LS_{1/4}$), ½ in crushed gravel (CG1), and Sand (S1). One large sample of these four aggregates was taken from APAC's facility in Meridian, MS and was used to produce all specimens for M21 to M38 in this report and also in the corresponding bio-rejuvenator's report. Two additional aggregates were available at CMRC that were used to produce mixes M39 to M49; Sand (S2) and ½ in crushed gravel (CG2). S1 and S2 would have originated from different sources, while CG1 and CG2 were from the same source and sampled at different times. CG2's gradation was altered from what would normally be supplied as ½ in crushed gravel from this source to meet the need of producing a DGA asphalt mixture from a single aggregate source. S2 was washed to remove almost all particles finer than a No. 200 sieve (0.075 mm).

Table 2.1. Virgin Aggregate Properties

Material	LS_{89}	$LS_{1/4}$	S1	CG1	S2	CG2
Passing 12.5 mm (%)	100	100	100	100	100	100
Passing 9.5 mm (%)	100	100	100	92	100	95
Passing No. 4 (%)	46	97	96	50	99	67
Passing No. 8 (%)	15	66	90	30	82	46
Passing No. 16 (%)	6	41	79	18	71	27
Passing No. 30 (%)	3	26	57	12	57	18
Passing No. 50 (%)	2	19	25	8	16	14
Passing No. 100 (%)	2	13	3	6	1	11
Passing No. 200 (%)	1.8	11.3	0.6	4.4	0.1	7.4
Bulk Specific Gravity (G_{sb})	2.726	2.705	2.610	2.379	2.560	2.385
Apparent Specific Gravity (G_{sa})	2.765	2.738	2.645	2.641	2.640	2.651
Percent Water Absorption (Abs.)	0.52	0.45	0.51	4.17	1.20	4.20

2.2.5 Recycled Materials

Reclaimed Asphalt Pavement (RAP) and Recycled Asphalt Shingles (RAS) were utilized in this report. In each case, one large sample was obtained in January of 2017 that was used throughout this work and throughout the corresponding bio-rejuvenators work. RAP was sampled from APAC's Meridian facility; the continuous grade of recovered binder was PG 105-7 and the average binder content was 4.6%. RAS was sampled from APAC's Columbus facility; the continuous grade of recovered bitumen was PG 209+24 and the average bitumen content was 17.1%. Table 2.2 shows representative aggregate gradations measured after bituminous material extractions.

Table 2.2. Representative Extracted Gradations of RAP and RAS

Material	RAP	RAS
Passing 19.0 mm (%)	100	100
Passing 12.5 mm (%)	99	100
Passing 9.5 mm (%)	94	100
Passing No. 4 (%)	66	98
Passing No. 8 (%)	43	95
Passing No. 16 (%)	32	77
Passing No. 30 (%)	25	57
Passing No. 50 (%)	17	51
Passing No. 100 (%)	11	42
Passing No. 200 (%)	8.9	33.8

2.3 Specimen Production

2.3.1 Blending Powdered CNC and CTO Materials Into PG 67-22 Binder

Freeze-dried, high lignin, cellulose nanocrystals (FD-HL-CNC) and crude tall oil (CTO) were used in conjunction with PG 67-22 binder. These additives were pre-blended into the bitumen as follows at a temperature of 163 ºC (325 ºF). If one additive was used in a mixture, one additive was blended into PG 67-22, and in cases where both were used in a mixture, both were blended into the same container of PG 67-22 binder, though they were blended one product at a time. Figure 2.3 shows the mixer, heating pot, and attachments used for blending activities.

The general expectation when blending these materials was that moderately elevated temperatures could help reduce viscosity and increase dispersion, keeping in mind the possible damage of elevated temperatures to CNCs. Shear thinning behavior was expected; i.e. for viscosity to be high until an equilibrium shear rate was reached. Mixing duration was 30 minutes at 163 ºC at 175 revolutions per minute (rpms). The paddle selected and shown in Figure 2.3 was believed to be sufficient to generate flow and produce dispersing. Particles sticking to the paddle was not a concern as the binder containers were fairly full and there was a fair amount of head over the mixing area so the paddle features were completely submerged and had a good vortex and could not draw in air. The CNCs were added slowly over a roughly five minute period so as not to overwhelm mixing (i.e. a few particles were added, a few seconds passed, a few more particles were added, and so forth).

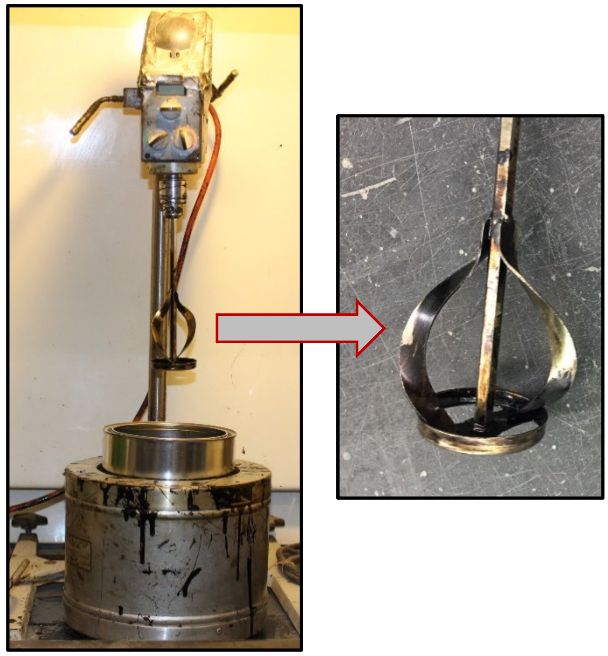


Figure 2.3. Blending FD-HL-CNC and CTO Into PG 67-22 Binder

Generally speaking, CNCs and/or CTO were blended into 1-gallon metal cans of PG 67-22 binder one day prior to mixing and compacting bituminous specimens. Each pre-weighted 1-gallon can of PG 67-22 was assigned to a mixture (i.e. cans were assigned to M23, M35, or M37 to M46) and heated to163 ºC. Once uniformly heated, additives were added while the can was in the heating pot to maintain temperature during blending.

After blending, binder was cooled to room temperature and stored overnight. Before adding blended binder to aggregates during mixing, the re-heated binder was stirred with a wooden dowel for approximately 45 seconds. Dosage rates that were used for incorporating all bio-based products into asphalt cement were calculated as shown in Hufft (2019) and are presented with all mixes later in this chapter.

2.3.2 Incorporating Aqueous CNC Materials Into Mixes

Aqueous, high lignin, cellulose nanocrystals (AQ-CNC) were incorporated into sand asphalt (SA) mixtures by diluting them with water before coating sand source S2 with the mixture while all ingredients were at 65°C (150 ºF). To enhance its coating capabilities, water was mixed with AQ-CNC in a ratio of 2:1 (i.e. two parts water to one part AQ) and then heated to 65°C in a water bath. This lower assessment temperature was determined due to the temperature sensitivity of AQ-CNC. The liquid mixture was added to the sand in grams of AQ per kg of sand in ratios of 5:1 and 10:1 to produce mixtures with approximately 1.1 and 2.2% CNC residue within the asphalt emulsion residue (actual CNC dosages are shown later). Preheated sand was treated in individual 5 kg batches by means of a 5-gallon mixing bucket and then air dried to a constant mass in pans prior to heating and mixing with emulsion.

For example, M48 was made to have approximately 1.1% CNC and was prepared by combining 25 g of AQ with 50 g of water in a metal tin. The tin was then covered and placed in a 65°C water bath until it reached mixing temperature. Thereafter, 5 kg of 65°C preheated sand was placed in a mixing bucket and the AQ/water combination was mixed into the sand until all sand particles were dampened. The coated sand was then placed into a pan and set aside to dry for several days. The mixing bucket was weighed both before the sand was added and after removing the treated sand to ensure that nothing was left in the bucket. From this process, it is assumed that the 5 kg of dried sand was coated with enough CNC so that the compacted specimen would contain approximately 1.1% CNC by the mass of the asphalt residue from the emulsion. At the conclusion of mixing sand and AQ, 25 g (in this example for M48) or 50 g (in the case of M49) of AQ coated 5 kg of sand S2. With an AQ-CNC moisture content of roughly 89%, approximately 2.75 grams (M48) or 5.5 grams (M49) of CNC residue remained after drying. A total of 368 grams of emulsion would be added to this 5 kg of sand, where the residue value was approximately 68%, or 250 grams of residual binder and 2.75 grams of residual CNC material is roughly 1.1% of the residual emulsion bitumen.

2.3.3 Specimen Mixing and Compaction

All DGA mixtures containing PG 67-22 asphalt binder were mixed or produced at 163°C (T_{Prod}) and compacted at 149°C. For these mixtures (M23, M35, M37, M38, and M39 to M46), virgin aggregates and fillers were batched and left in an oven to heat to mixing temperature overnight. Two hours prior to mixing, any needed RAP or RAS was added to the heated aggregates to control additional bitumen aging. Mixing was performed using either a 10-gallon or a 5-gallon metal bucket mixer. Figure 2.4 shows the 10-gallon mixer. Prior to compaction, the freshly mixed material was short term oven-aged (STOA) for 90 minutes at the required compaction temperature. Specimens were then individually compacted using a Superpave Gyratory compactor (SGC). DGA specimens were compacted to a target height of 115 mm and the number of gyrations needed to do so was recorded (N_{gyr}). After mixing and compacting, specimen bulk specific gravity (G_{mb}) was measured in accordance with AASHTO T331 (vacuum sealing) to obtain air void (V_a) values when maximum mixture specific gravity (G_{mm}) was measured according to AASHTO T209. The target V_a for DGA specimens was 7.5%. Actual values for the 132 specimens evaluated in Chapter 3 were 7.1 to 8.1% with an average of 7.5%. Note that the aforementioned procedures were used to produce specimens for testing. Section 2.6 describes preliminary efforts that were used to establish needed proportioning with which these procedures could be implemented.

Figure 2.4. Mixing Process and Equipment

All SA mixtures containing CRS-2P emulsion (M47 to M49) were mixed and compacted at 65°C (150 ºF). Emulsion and sand pre-coated with CNCs were both heated to 65 ºC, and production procedures generally followed those for DGA. The primary exceptions were that SA specimens were compacted to 125 gyrations with an average height of just under 130 mm, they were not exposed to STOA, and all mixing tools/molds were at room temperature. Air voids (V_a) were recorded for all SA specimens.

2.4 Specimen Handling

After specimens were produced and their air voids had been measured, they were handled prior to testing in one of three manners: unaged, laboratory conditioned, or field aged. Laboratory conditioning is intended to simulate field aging. Each of these procedures are described in the following sub-sections.

2.4.1 Unaged Specimens

Unaged specimens were produced, stored in ambient air conditioned laboratory conditions away from direct sunlight. Unaged specimens are sometimes referred to as virgin specimens, unaged specimens, or unconditioned specimens. Their purpose is to represent properties of the bituminous paving material immediately after they are placed on the roadway. In their unaged state, asphalt pavements are generally the most resistant to raveling, cracking, or otherwise most resistant to weathering, but they are also generally the least resistant to rutting under traffic.

2.4.2 Laboratory Conditioned Specimens

One conditioning protocol (CP) that was presented in Smith and Howard (2019) was used in this study; this protocol is often referred to as CP7. Three conditioning mechanisms were used to simulate aging: oven conditioning at 85°C for 5 days, hot water bath conditioning at 64°C, and a freeze-thaw (FT) cycle. Room temperature specimens were placed in a preheated force-draft oven and left to age for 120 ± 0.5 hours. After conditioning was completed, specimens were cooled to room temperature with the oven turned off and the door opened. Specimens were then vacuum saturated within a range of 70 to 80% of AASHTO T166 measured V_a volume. Specimens were then stored in submerged room temperature water before being transferred to a 64°C preheated water bath for hot water conditioning for 14 days. When hot water conditioning was completed, specimens were again cooled to room temperature while still submerged in water.

Following hot water conditioning was a single FT cycle. Specimens were transferred directly from the room temperature water to a prechilled freezer. After all specimens were loaded into the freezers, the doors were closed for 24 hours to allow the specimens to freeze to -22°C. The freezer was then turned off after 24 hours and specimens were thawed. Thereafter, specimens air dried for at least 42 days prior to testing. Smith and Howard (2019) showed CP7 simulated on the order of 5 years of aging in Mississippi's climate.

2.4.3 Field Aged Specimens

Field aging for this overall body of work (CNCs and bio-rejuvenators) occurred over a three-year period from July 3, 2018 to July 3, 2021. Mixes M21 to M36 were field aged between July of 2018 to July of 2020, and M37 to M49 were field aged between July of 2019 and July of 2021. There were 256 field aged M21 to M36 specimens, and out of these specimens only 6 were relevant to this work (the rest were for bio-rejuvenators work); M23 and M35 field aged for 1 year (1F). These 6 specimens served dual use in this report and also in the companion bio-rejuvenators report where all 256 M21 to M36 field aged specimens are accounted for. There were 72 field aged M37 to M49 specimens, all of which were evaluated in this report. For reference, a total of 267 specimens were put onto the test section to age on July 3, 2019, only 72 of them are relevant to this report, though some of the other specimens are visible in the Figure 2.5 and Figure 2.6 photographs showing field aging. For reference, 63 mixes (M01 to M63) have been field aged at this site as of June 2023, and only a portion of these mixes are relevant to this report.

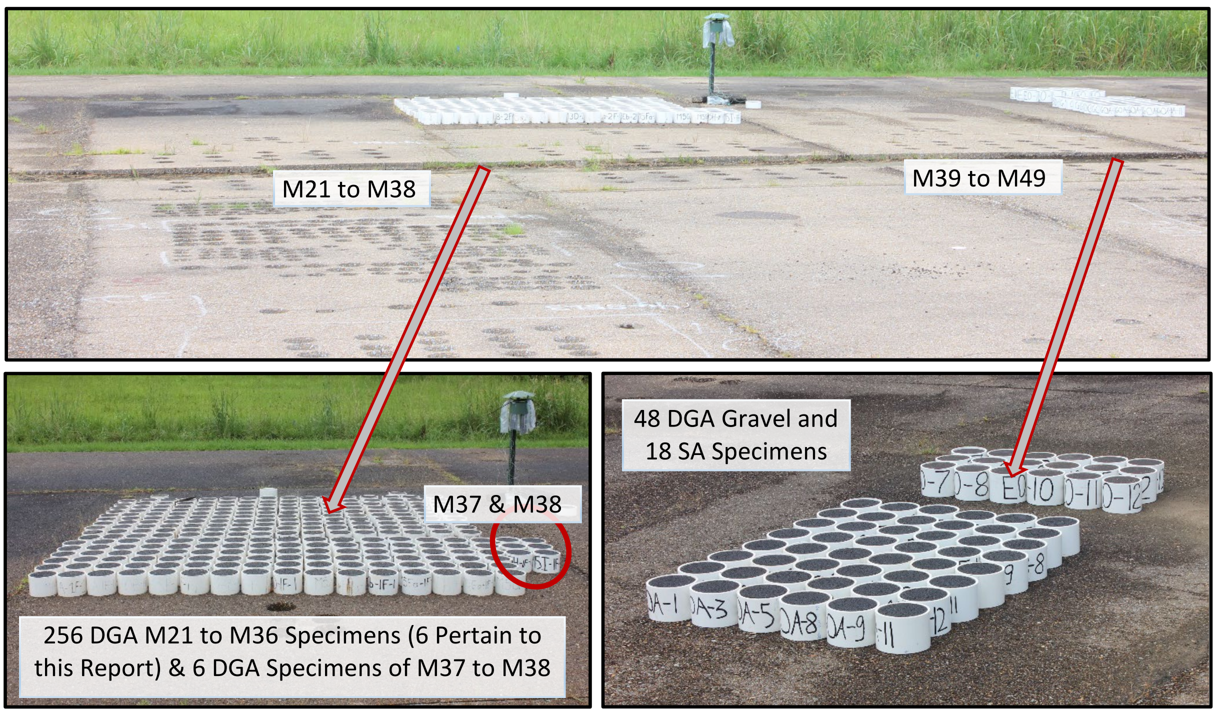


Figure 2.5. Field Aging Photos at Initiation of Aging – Overall Views – July 3, 2019

Field aging occurred for 1 year (1F) or 2 years (2F). Field aging occurred at APAC's Columbus, MS facility which is approximately 44 km from MSU's campus. This aging site has been used for over a decade as of this report's date and has aged several dozen mixtures. This site is often referred to as the Columbus Parking Lot (CPL).

All specimens were aged in PVC sleeves so that only specimen tops were subjected to direct sunlight and weathering. PVC sleeves were made by slicing standard 6 inch (152 mm) diameter PVC pipe to 115 to 130 mm tall depending on the specimen. During aging, the site experienced significant flooding for approximately four days from February 23 to February 27, 2019. No specimens were damaged, though some PVC sleeves needed replacement.

Figure 2.6. Field Aging Photos – Local Views

2.5 Mechanical Property Testing

Cantabro Mass Loss (CML) testing was performed according to what is currently AASHTO T401 protocols; AASHTO TP108 would have been the designation at the time these experiments were conducted. A compacted asphalt specimen is placed into an LA Abrasion drum absent steel spheres at 25 ºC and is subjected to 300 drum revolutions. Mass loss (ML) is the change in specimens mass divided by the original mass. Cox et al. (2017) and Doyle and Howard (2011) provide more information on CML testing of compacted asphalt.

2.6 Preliminary Testing for Mixture Proportioning

Prior to fabricating the specimens described for test matrices in the following section, some preliminary testing was performed. There were three general categories of DGA produced in this work and one general category of SA produced in this work. The next section provides specific test matrices, while this section describes preliminary efforts to establish mixture proportions that were ultimately evaluated in Chapter 3.

Mixes 23, 35, 37, and 38 were patterned after traditional DGA where a blend of different aggregates was utilized. The companion bio-products work provides more information on this mixture category. This category of mixture is referred to as DGA-B-RAS where B is used to denote a blend of aggregates and RAS denotes the incorporation of shingles. M23 is very close to the manner in which a paving contractor uses this mixture on a routine basis. The actual design has a total binder content (P_b) of 5.9%, whereas 6.0% was used herein to be suitable for four mixes based on preliminary testing for the companion bio-products work. The SGC design gyrations (N_{des}) for this mixture was 50 and would have achieved roughly 4% air voids at this compactive effort.

Mixes 39, 41, 43, and 45 were produced with one gravel aggregate (CG2), BHD as filler, and a P_b of 7.5%. This P_b was loosely based on work in Hansen and Howard (2020) where an all gravel mixture from this source was used having a water absorption of 4.2% had P_b values ranging from 8.0 to 8.3%. This work elected to use a modestly lower value of 7.5% after exploring a few gradations (the gradation selected was the finest gradation evaluated) where 5% air voids were achieved at N_{des} of 65. For purposes of investigating CNC effects in a mixture with limited variables, these proportions were deemed reasonable. These four mixtures were a category labeled DGA-G, where G refers to the gravel aggregates.

Mixes 40, 42, 44, and 46 were produced in a similar manner to mixes 39, 41, 43, and 45, except that 5% RAS substituted some of the gravel aggregates and virgin PG 67-22 binder. The same total binder content was used (7.5%), but only 6.7% was virgin binder, while the remaining binder came from RAS. These four mixtures were a category labeled DGA-G-RAS to denote the inclusion of shingles.

To the author's knowledge, the efforts in this research were the first attempts to mix CNC's with emulsion and sand (S2). To gage proportions, two preliminary cases were evaluated. Case 1 made use of 5,000 grams of sand, 150 grams of emulsion (102 grams of bituminous residue), 150 grams of water, and 0 grams of AQ CNC. Case 2 made use of 5,000 grams of sand, 150 grams of emulsion (102 grams of bituminous residue), 75 grams of water, and 75 grams of AQ CNC (8.25 grams of residual CNC). Case 2 had a CNC dosage of roughly 8.1%, and as seen in Figure 2.7, this amount of CNC with only 102 grams of bituminous residue did not produce a stable specimen. The Case 1 specimen held its shape, but there was noticeable lack of sand coating. These experiments were performed where all ingredients were heated to 150 °F, mixed, and immediately compacted with 30 gyrations of a Superpave Gyratory Compactor. All mixing tools, the mixing bucket, and the compaction mold were at room temperature. The findings from these preliminary experiments led to an increase in emulsion content, a decrease in CNC's content, and pre-coating the sand with CNC's where water could evaporate prior to emulsion incorporation for SA specimens.

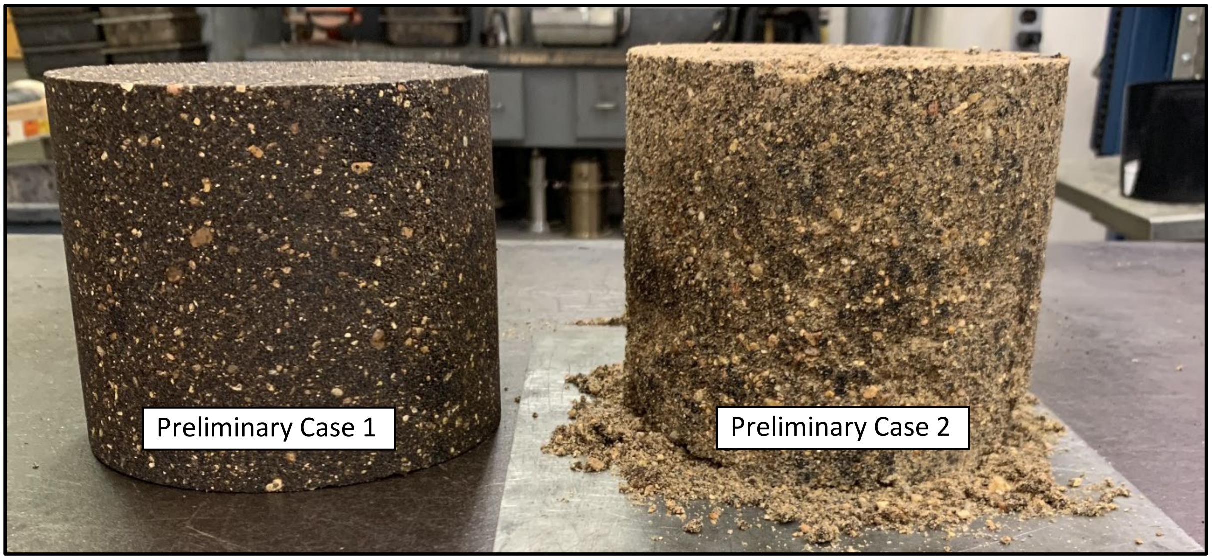


Figure 2.7. Preliminary Sand Asphalt Proportioning Exercises

2.7 Test Matrices and Mixture Proportions

Tables 2.3 to 2.5 summarize the final mixture proportions used to produce the 168 specimens analyzed in Chapter 3. Table 2.3 summarizes aggregate proportions where most terms were defined in the materials descriptions provided earlier. Table 2.4 summarizes binder and additive proportions. Binder contents provided by RAP ($P_{b(RAP)}$), RAS ($P_{b(RAS)}$), and PG 67-22 asphalt cement ($P_{b(AC)}$) are provided for each DGA mixture. These three binder contents sum to the total binder content (P_b) of a DGA mixture and are on a mixture mass basis. All binder in SA mixtures came from CRS-2P emulsion, which is denoted $P_{b(Em)}$ and equates to P_b for these mixtures because no RAP, RAS, or PG 67-22 was present in SA. All SA binder terms in Table 2.4 are also on a mixture mass basis.

Table 2.5 describes the test matrix that is analyzed in Chapter 3. This test matrix is organized into four data groups. Each group has a different combination of characteristics. The first group (DGA-B-RAS) uses the same general blend as the bio-rejuvenators blend and represents a very realistic asphalt mixture used in present day. The second group makes use of only gravel aggregates; gravel aggregates can pose problems for some mixes, so isolating variables and investigating gravel in the presence of CNC's was chosen. The third group only makes use of gravel aggregates, but adds recycled shingles as well. The fourth group is only sand asphalt to evaluate aqueous CNC's in conjunction with asphalt emulsions.

Table 2.3. Mixture Properties: Aggregates, Fillers, Recycled Materials, and Blend Gradations

Mix ID	Aggregate and Filler Proportions[1] (%)							Recycled Material (%)		Percent Passing of Blend[5]			
	CG1	CG2	LS[2]	S1	S2	HL	BHD	RAP[1]	RAS[3]	12.5 mm	No. 8	No. 30	No. 200
M23	30	0	38.5	5.6	0	1	0.5	20	5	100	38	17	7.5
M35	30	0	38.5	5.6	0	1	0.5	20	5	100	38	17	7.5
M37	30	0	38.5	5.6	0	1	0.5	20	5	100	38	17	7.5
M38	30	0	38	5.6	0	1	0.5	20	5	100	38	17	7.5
M39	0	97.6	0	0	0	0	2.4[4]	0	0	100	47	20	9.6
M40	0	93.2	0	0	0	0	2.4	0	5	100	50	21	10.8
M41	0	97.6	0	0	0	0	2.4	0	0	100	47	20	9.6
M42	0	93.2	0	0	0	0	2.4	0	5	100	50	21	10.8
M43	0	97.6	0	0	0	0	2.4	0	0	100	47	20	9.6
M44	0	93.2	0	0	0	0	2.4	0	5	100	50	21	10.8
M45	0	97.6	0	0	0	0	2.4	0	0	100	47	20	9.6
M46	0	93.2	0	0	0	0	2.4	0	5	100	50	21	10.8
M47	0	0	0	0	100	0	0	0	0	100	82	57	0.1
M48	0	0	0	0	100	0	0	0	0	100	82	57	0.1
M49	0	0	0	0	100	0	0	0	0	100	82	57	0.1

1: All aggregate and filler proportion values and RAP dosage values are percentages of total dry aggregate mass.
2: LS is combination of LS_{89} and $LS_{1/4}$ limestone sources.
3: Dosage rate based on total mix mass. For reference, 5% RAS was 4.4% of aggregate blend.
4: Roughly 25% of the fine particles in M39 to M46 were BHD to simulate dust return in a plant and because fine gravel particles were limited
5: M23 to M46 would classify as 9.5 mm nominal maximum aggregate size (NMAS) blends.

Table 2.4. Mixture Properties: Binders and Additives

Mix ID	Binders P_b	$P_{b(RAP)}$	$P_{b(RAS)}$	$P_{b(AC)}$	$P_{b(Em)}$	Type	Additives CTO[1]	FD[2]	AQ[3]
M23	6.0	0.9	0.8	4.3	0.0	PG 67-22	0.0	0.0	0.0
M35	6.0	0.9	0.8	4.3	0.0	PG 67-22	5.0	0.0	0.0
M37	6.0	0.9	0.8	4.3	0.0	PG 67-22	0.0	1.0	0.0
M38	6.0	0.9	0.8	4.3	0.0	PG 67-22	5.0	1.0	0.0
M39	7.5	0.0	0.0	7.5	0.0	PG 67-22	0.0	0.0	0.0
M40	7.5	0.0	0.8	6.7	0.0	PG 67-22	0.0	0.0	0.0
M41	7.5	0.0	0.0	7.5	0.0	PG 67-22	0.0	1.0	0.0
M42	7.5	0.0	0.8	6.7	0.0	PG 67-22	0.0	1.0	0.0
M43	7.5	0.0	0.0	7.5	0.0	PG 67-22	5.0	0.0	0.0
M44	7.5	0.0	0.8	6.7	0.0	PG 67-22	5.0	0.0	0.0
M45	7.5	0.0	0.0	7.5	0.0	PG 67-22	5.0	1.0	0.0
M46	7.5	0.0	0.8	6.7	0.0	PG 67-22	5.0	1.0	0.0
M47[3]	4.8	0.0	0.0	0.0	4.8	CRS-2P	0.0	0.0	0.0
M48	4.8	0.0	0.0	0.0	4.8	CRS-2P	0.0	0.0	1.1
M49	4.8	0.0	0.0	0.0	4.8	CRS-2P	0.0	0.0	2.2

1: Dosage rate is a percentage of total binder mass P_b
2: Dosage is a percentage of PG 67-22 mass $P_{b(AC)}$
3: Dosage is a percentage of CNC residue by mass of emulsion residue. M47 to M49 had 368 g of emulsion (250 g of residue) added to 5,000 g of sand, or 250 g bitumen and 0, 2.75, or 5.5 g of CNC residue in a total mass of 5,250 to 5,256 g

Table 2.5. Test Matrix

Mix ID	Data Group	Additive(s)	Dosage	CML Replicates Unaged	CP7	1F	2F
M23	DGA-B-RAS	---	---	3	3	3	---
M35	DGA-B-RAS	CTO	5%	3	3	3	---
M37	DGA-B-RAS	FD	1%	3	3	3	---
M38	DGA-B-RAS	CTO, FD	5%, 1%	3	3	3	---
M39	DGA-G	---	---	3	3	3	3
M43	DGA-G	CTO	5%	3	3	3	3
M41	DGA-G	FD	1%	3	3	3	3
M45	DGA-G	CTO, FD	5%, 1%	3	3	3	3
M40	DGA-G-RAS	---	---	3	3	3	3
M44	DGA-G-RAS	CTO	5%	3	3	3	3
M42	DGA-G-RAS	FD	1%	3	3	3	3
M46	DGA-G-RAS	CTO, FD	5%, 1%	3	3	3	3
M47	SA	---	---	3	3	3	3
M48	SA	AQ	1.1%	3	3	3	3
M49	SA	AQ	2.2%	3	3	3	3

CHAPTER 3 – TEST RESULTS

3.1 Overview of Test Results

Table 3.1 provides results of all 168 specimens tested for Cantabro Mass Loss (CML) organized by data group, while tables 3.2 and 3.3 provide gyratory compaction results. Values shown in Table 3.1 are the average of three replicates. These 168 specimens are evaluated by data groups that are described in sections 2.6 and 2.7. Thereafter, discussion of major findings is provided in a standalone section.

Table 3.1. CML Test Results

Mix ID	Data Group	Additive(s)	Dosage	CML (%)			
				Unaged	CP7	1F	2F
M23	DGA-B-RAS	---	---	16.0	28.9	20.7	---
M35	DGA-B-RAS	CTO	5%	19.0	31.4	24.8	---
M37	DGA-B-RAS	FD	1%	17.2	26.9	19.2	---
M38	DGA-B-RAS	CTO, FD	5%, 1%	18.6	34.7	23.9	---
M39	DGA-G	---	---	8.0	17.4	12.9	13.8
M43	DGA-G	CTO	5%	7.3	17.8	16.4	16.8
M41	DGA-G	FD	1%	7.4	21.1	13.1	14.0
M45	DGA-G	CTO, FD	5%, 1%	8.4	16.6	16.1	16.6
M40	DGA-G-RAS	---	---	10.0	20.1	13.9	16.1
M44	DGA-G-RAS	CTO	5%	11.3	22.5	16.5	18.5
M42	DGA-G-RAS	FD	1%	10.6	22.1	15.2	16.2
M46	DGA-G-RAS	CTO, FD	5%, 1%	10.2	23.5	18.3	17.6
M47	SA	---	---	11.2	81.0	11.9	17.3
M48	SA	AQ	1.1%	12.8	76.6	13.1	14.1
M49	SA	AQ	2.2%	4.9	43.8	9.7	11.2

Table 3.2. Gyratory Test Results for Specimens Compacted to 115 mm Height

Mix ID	Data Group	Additive(s)	Dosage	n	N_{gyr}	
					Avg	Stdev
M23	DGA-B-RAS	---	---	9	25	2.1
M35	DGA-B-RAS	CTO	5%	9	22	3.5
M37	DGA-B-RAS	FD	1%	9	27	4.6
M38	DGA-B-RAS	CTO, FD	5%, 1%	9	22	3.5
M39	DGA-G	---	---	12	32	5.3
M43	DGA-G	CTO	5%	12	38	11.8
M41	DGA-G	FD	1%	12	29	4.7
M45	DGA-G	CTO, FD	5%, 1%	12	37	10.0
M40	DGA-G-RAS	---	---	12	23	3.4
M44	DGA-G-RAS	CTO	5%	12	23	2.7
M42	DGA-G-RAS	FD	1%	12	27	5.3
M46	DGA-G-RAS	CTO, FD	5%, 1%	12	24	3.0

--- n is the number of replicates, Avg is the average, and Stdev is the standard deviation.

Table 3.3. Gyratory Test Results for Specimens Compacted to 125 Gyrations

Mix ID	Data Group	Additive(s)	Dosage	n	Compacted Height (mm) Min	Max	Avg
M47	SA	---	---	12	126.7	130.1	128.0
M48	SA	AQ	1.1%	12	126.7	129.0	128.3
M49	SA	AQ	2.2%	12	126.9	129.9	128.6

--- Min is the minimum value and Max is the maximum value.

3.2 DGA Results for Traditionally Designed Mixes With RAS (DGA-B-RAS)

It should be noted that field aging was offset by one year for this group of specimens. M23 and M35 were field aged from 2018 to 2019, while M37 and M38 were field aged from 2019 to 2020. This is not believed to be of first order importance, but was deemed noteworthy.

The gyratory compaction results shown in Table 3.2 do not show large differences in compactive effort for any of these four mixes. Air voids of any one specimen in this data group were fairly tightly grouped, ranging from 7.2 to 8.1%. Average values for any one mix ranged from 7.5 to 7.8%, which is sufficiently tightly grouped to neglect air voids during additives assessment.

An Analysis of Variance (ANOVA) was performed at a 5% level of significance for a t-grouping of means for unaged and CP7 conditioned specimens (Table 3.4). When unaged, all additives increased mass loss (undesirable) to a level they were in a different statistical t-grouping than the control mix without additives. When aged, FD CNC, when used as the only additive, outperformed the control mixture in CP7 conditioning and after 1 year of field aging.

Table 3.4. Results of t-grouping for DGA-B-RAS Data Group

Treatment	Mix (Additive(s))	t-grouping	ML (%)
Unaged	M35 (CTO)	A	19.0
	M38 (CTO, FD)	A	18.6
	M37 (FD)	A B	17.2
	M23 (---)	B	16.0
CP7	M38 (CTO, FD)	A	34.7
	M35 (CTO)	A	31.4
	M23 (---)	A	28.9
	M37 (FD)	A	26.9

One year of field aging (1F) produced comparable trends to CP7 conditioning. In CP7 and 1F, the two mixes containing CTO performed the worst, and the mix with only FD CNC performed the best. There were not large differences between the control and FD CNC, but overall, FD CNC (M37) performed the best in this group of mixes by a modest margin.

Of secondary interest to the current work, but of overall interest to simulating field aging is how many years of field aging were simulated by CP7 in these mixes containing CNCs. A linear rate of mass loss with time was assumed in the assessment performed herein, where the results can be found in Table 3.5. The term ΔML is the increase in mass loss (%) per year of field aging, and the years of field aging simulated by CP7 were found by taking the difference between CP7 and unaged mass losses, and dividing by ΔML. As seen, roughly 2 to

5 years of field aging were simulated by CP7, which is somewhat lower than the roughly 5 years reported by Smith and Howard (2019).

Table 3.5. Amount of Field Aging Simulated by CP7 for DGA-B-RAS Data Group

Mix	ΔML (Percent per Year)	Years of Aging Simulated by CP7
M23	4.7	2.8
M35	5.8	2.1
M37	2.0	4.9
M38	5.3	3.0

3.3 DGA Results for all Gravel Mixes Without RAS (DGA-G)

The gyratory compaction results shown in Table 3.2 show, on average, 5 to 6 additional gyrations being required to compact specimens containing CTO relative to control specimens without additives. The mix containing only FC CNC's required three less gyrations than the control. In general, compaction with less required energy is desirable so long as a mixture can still be stable under vehicle traffic. Air voids of any one specimen in this data group were fairly tightly grouped, ranging from 7.2 to 8.1%. Average values for any one mix ranged from 7.5 to 7.6%, which is sufficiently tightly grouped to neglect air voids during additives assessment.

Tables 3.6 and 3.7 summarize ANOVA results and years of aging simulated by CP7 where evaluations were performed in the same manner as Section 3.2. There were no statistical differences detected for this data group. Trends were not drastically different for this data group relative to DGS-B-RAS (Section 3.2). When unconditioned, the control with no additives was an intermediate performer. When CP7 conditioned, CTO and FD CNC added together (M45) to one mixture was the best performer, whereas, in Section 3.2 this combination was among the worst performance (Mix 38). CP7 was the only treatment where CTO and FD added together produced a desirable result. When all four treatments and both mixes with CTO are viewed together, the mixes containing CTO had poorer performance than those that did not have CTO. FD CNC (M41), overall, performed comparably to the control (M39) in this all gravel mixture. Note that the CP7 ML value of 21.1% for M41 was meaningfully affected by one of the three measurements (16.6, 18.8, and 27.7). If the 27.7% value is removed, the average mass loss reduces to 17.7% which is very similar to the control mixture with no additives. The amount of field aging simulated by CP7 was roughly 2 to 4 years, which is somewhat lower than the roughly 5 years reported by Smith and Howard (2019).

Table 3.6. Results of t-groupings for DGA-G Data Group

Treatment	Mix (Additive(s))	t-grouping	ML (%)
Unaged	M45 (CTO, FD)	A	8.4
	M39 (---)	A	8.0
	M41 (FD)	A	7.4
	M43 (CTO)	A	7.3
CP7	M41 (FD)	A	21.1
	M43 (CTO)	A	17.8
	M39 (---)	A	17.4
	M45 (CTO, FD)	A	16.6

Table 3.7. Amount of Field Aging Simulated by CP7 for DGA-G Data Group

Mix	ΔML (Percent per Year)	Years of Aging Simulated by CP7
M39	2.9	3.2
M43	4.8	2.2
M41	3.3	4.2
M45	4.1	2.0

3.4 DGA Results for all Gravel Mixes With RAS (DGA-G-RAS)

The gyratory compaction results shown in Table 3.2 do not show large differences in compactive effort for any of these four mixes. Air voids of any one specimen in this data group were fairly tightly grouped, ranging from 7.1 to 7.7%. Average values for any one mix ranged from 7.3 to 7.5%, which is sufficiently tightly grouped to neglect air voids during additives assessment.

Tables 3.8 and 3.9 summarize ANOVA results and years of aging simulated by CP7 where evaluations were performed in the same manner as Section 3.2. The primary statistical observation was that the control mixture with no additives was the best performer after CP7 conditioning and the mix containing CTO and FD CNC was the worst performer after CP7 conditioning. Overall trends, however, were fairly clear for this data group. The control mix without additives (M40) performed the best, followed the mix containing FD CNC (M42). Mixes with CTO were again the worst performing mixes. The amount of field aging simulated by CP7 was roughly 3 to 4 years, which is somewhat lower than the roughly 5 years reported by Smith and Howard (2019).

Table 3.8. Results of t-groupings for DGA-G-RAS Data Group

Treatment	Mix (Additive(s))	t-grouping	ML (%)
Unaged	M44 (CTO)	A	11.3
	M42 (FD)	A	10.6
	M46 (CTO, FD)	A	10.2
	M40 (---)	A	10.0
CP7	M46 (CTO, FD)	A	23.5
	M44 (CTO)	A B	22.5
	M42 (FD)	A B	22.1
	M40 (---)	B	20.1

Table 3.9. Amount of Field Aging Simulated by CP7 for DGA-G-RAS Data Group

Mix	ΔML (Percent per Year)	Years of Aging Simulated by CP7
M40	3.1	3.3
M44	3.6	3.1
M42	2.8	4.1
M46	3.7	3.6

3.5 SA Results for Mixes Without RAS (SA)

Sand asphalt mixes were produced with emulsified asphalt and aqueous CNC's, and as such were assessed independently relative to sections 3.2 to 3.4 where dense graded asphalt was evaluated in the same overall manner. Final height (Table 3.3) and air voids data for these mixes suggest the CNC's modestly inhibited compaction as the compacted height for mixes 47 to 49 increased as a function of AQ content. Air voids (V_a) measured on these specimens supported the height observations as the average air voids for M47 were 12.4% (Stdev of 0.7%), while the average air voids for M48 and M49 were 13.0% (Stdev of 0.6%) and 13.0% (Stdev of 0.8%), respectively. Air void differences were not considered when comparing Cantabro Mass Loss values.

When compared to the control mixture, 1.1% AQ dosage behaved in a comparable manner. However, doubling the dosage to 2.2% led to fairly drastic behavior improvements for all treatments. Quantification of the benefits of the 2.2% AQ dosage is not feasible from these sand asphalt mixes, but the potential benefits to performance are very clear given the large reduction in mass loss observed. A more comprehensive study should be considered to evaluate bituminous mixes stabilized with emulsion that incorporate aqueous CNCs. The behavior differences between M47 and M49 are the most impactful finding in this report.

One note of relevance is that CP7 conditioning meaningfully damaged these sand asphalt specimens (Figure 3.1). All nine specimens were able to be tested, but there were large and obvious cracks along several of the specimens. These cracks likely affected the magnitude of the values measured and reported, but any damage during the protocol is realistic of damage that could occur in service and all mixtures received identical treatment.

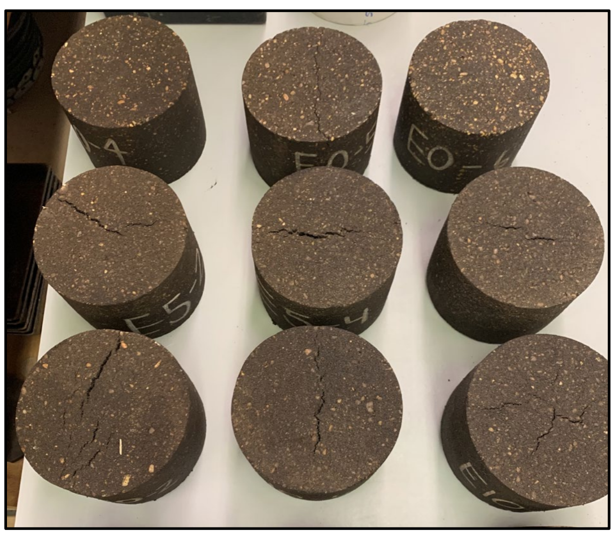


Figure 3.1. Visual Damage to Sand Asphalt During CP7 Conditioning

3.6 Discussion of Results

Figure 3.2 compares all Cantabro Mass Loss data for dense graded asphalt by way of equality plots. Given lower ML values are desired, a slope less than 1.00 suggests a given additive or combination of additives performed at a level above the control mixture without any additives. A line of equality (i.e. y = x) is shown and regression through the origin was utilized.

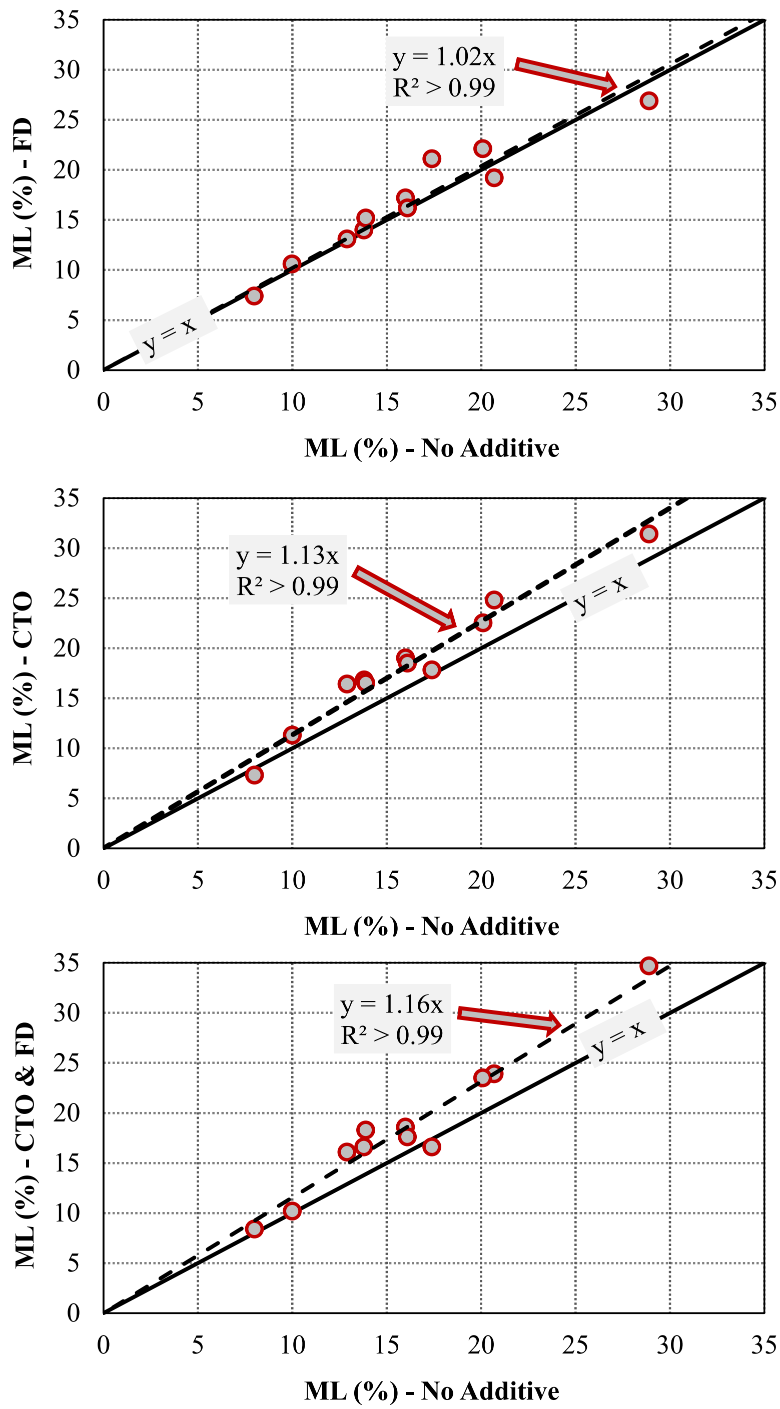


Figure 3.2. Collective Comparison of Additives in Dense Graded Asphalt

Figure 3.2 shows that no additive or combination, overall, performed better than the control mixture without additives. Freeze-dried (FD) CNC's had a slope of 1.02, which indicates a slight increase in mass loss due to their addition. Given the nature of the experiments performed, a slope this close to 1.00 would, overall, suggest that FD CNC's performed in a manner comparable to, perhaps slightly worse than, control mixtures without additives. When crude tall oil (CTO) was added, performance decreased sharply. A slope of 1.13 is a fairly clear indication that the CTO, as added to these mixtures, had a negative impact on mechanical behavior. Interestingly, the combination of FD and CTO had a slope of 1.16, which is almost identical to the sum of the increase in slopes of the two materials individually relative to the control (i.e. 0.02 + 0.13 = 0.15). Figure 4.2 clearly shows CTO, as added to these mixtures, as the primary factor leading to undesirable behavior relative to control mixes.

CHAPTER 4 – SUMMARY AND CONCLUSIONS

4.1 Summary

This report's primary objective was to assess cellulose nanocrystals (CNCs) within bituminous mixtures. Brittleness potential as measured by Cantabro Mass Loss testing was the primary evaluation mechanism; 168 specimens were Cantabro tested in addition to preliminary specimens produced earlier in the project for exploratory purposes. Compacted specimens were treated one of four ways prior to testing: 1) no treatment controls that were unaged; 2) laboratory conditioned and exposed to oxidation, moisture, and freeze-thaw conditions; 3) field aged for one year; and 4) field aged for two years. The specimens can generally be divided into two categories. The first category was dense graded asphalt produced with a few different combinations at 163 ºC temperatures in conjunction with freeze dried CNC's. The second category was sand asphalt produced with emulsions and aqueous CNCs at 65 ºC. This work did not investigate economic or logistical/production factors, but rather focused on pilot level evaluations relative to the potential of CNC's to improve brittleness tendencies of bituminous mixtures.

4.2 Conclusions

This study led to the following conclusions.

1. Freeze dried CNCs, overall, performed in a manner comparable to, perhaps slightly worse than, control mixtures without additives for dense graded asphalt.
2. Aqueous CNCs, at some dosage rates, led to drastic behavior improvements for sand asphalt stabilized with emulsion across a range of treatments spanning unaged, combined effects laboratory conditioning, and field aging of up to two years.
3. Crude tall oil, as used in this report, decreased performance in dense graded asphalt mixtures.

4.3 Recommendations

This study led to the following recommendations.

1. Aqueous CNCs used in conjunction with asphalt emulsion to produce mixtures at temperatures on the order of 65 ºC had technical merit and are recommended for a more comprehensive investigation, and might be worthy of an invention disclosure assessment.
2. Freeze dried CNCs did not show considerable potential in traditional plant mixed asphalt settings (e.g. mixing temperatures on the order of 163 ºC). It is recommended that these products be assessed for alternative applications.

CHAPTER 5 - REFERENCES

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