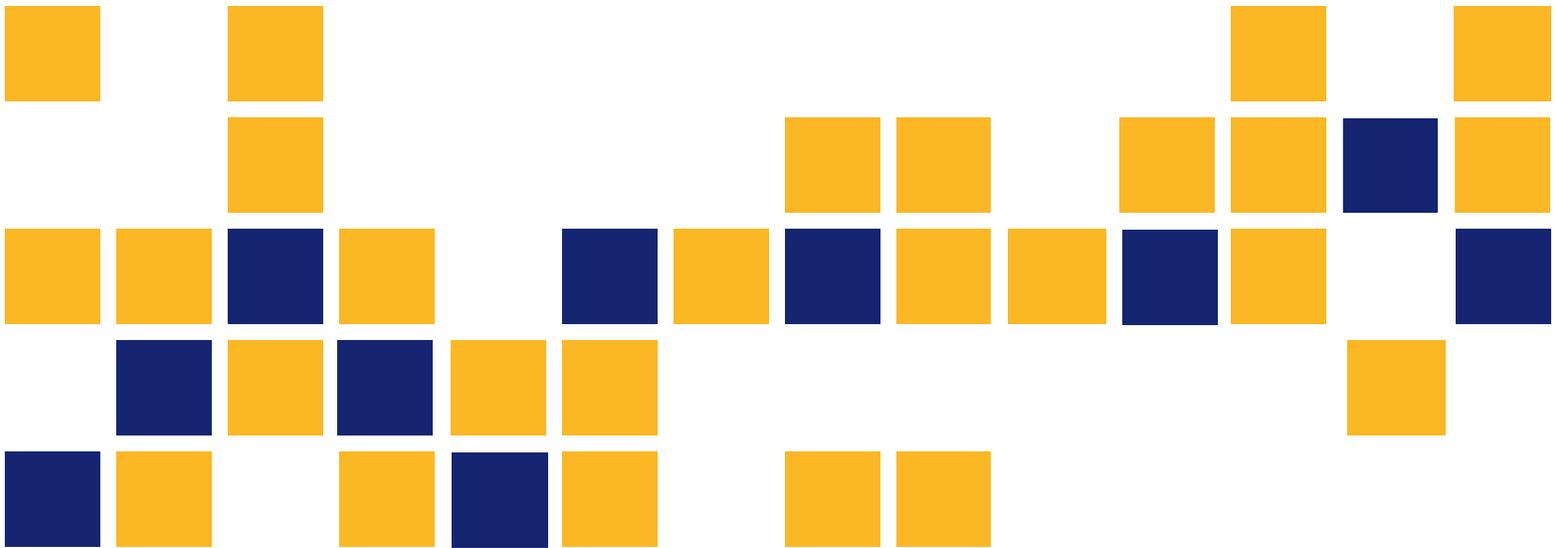


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Investigation of the Impact of Nanotechnology on the Freeze-Thaw Durability of Concrete Containing D-Cracking Aggregates

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Final Report

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Abstract

Freezing and thawing damage is the most common cause of distress in Kansas pavements. Many locally available aggregates in Kansas do not meet current standards for use in concrete pavements because of poor freeze-thaw durability. The use of nanotechnology to potentially improve the performance of aggregates with poor freeze-thaw durability in concrete was explored. Aggregates were impregnated by silica, alumina, and titanium nanoparticles, sealed with three different sealers, or soaked in a latex solution before inclusion in concrete mixtures and testing in freezing and thawing. Additionally, a powdered latex additive was added as a cement additive to an additional concrete mixture. While the nanoparticles, two sealers, and soaking in the latex solution slightly improved the performance of concrete in a freezing and thawing environment, none of the treatment methods improved the performance significantly enough for inclusion in Kansas pavements.

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Chapter 1: Introduction

1.1 Research Background

Freezing and thawing damage of limestone aggregates in concrete pavements costs millions of dollars in repairs annually in Kansas. Several cities in Kansas have banned the use of limestone aggregates in concrete, and require hard aggregates from neighboring states to be used. For some locations in Kansas, it may not be economical to rail in hard aggregates. The Kansas Department of Transportation (KDOT) has developed rigorous testing procedures for limestone aggregate use in concrete. Several new technologies for slowing down water adsorption rates of porous solids and improving concrete properties have been developed in recent years. Nanoparticles have been shown to improve the mechanical behavior and chloride permeability resistance of concrete. They have also been suggested to potentially help improve the resistance of the concrete to alkali-silica reaction (Sanfilippo, Munoz, Tejedor, Anderson, & Cramer, 2010). It was hypothesized that impregnation of limestone aggregates with nanoparticles could serve as nucleation sites for ice formation, or could potentially block pores to limit water access. Silane and other molecules that increase the material hydrophobicity or decrease water absorption rates could also improve concrete freeze-thaw behavior by reducing the degree of saturation of the aggregates.

Work was undertaken as a pilot study to determine if the behavior of limestone aggregates in concrete pavement could be improved through the use of nanotechnology. Nanoparticles, sealers, and other additives were used to lower the concrete absorption rate. Concrete beams were made and tested in this study according to the concrete beam freeze-thaw method KTMR-22 (2006).

1.2 Research Objectives

The research objectives of this study were as follows:

- To determine if impregnation of aggregates with poor freeze-thaw durability by nanoparticles could improve the behavior of concrete made with the aggregates in freezing and thawing conditions.

- To determine if penetrating sealers or latex additives could be used to treat and consequently improve the performance of concrete containing aggregates with poor freeze-thaw durability.

1.3 Scope of Research

Aggregates with a record of poor freeze-thaw durability in concrete were treated with nanoparticles, sealers, and latex additives before using them in concrete mixtures. The beams were tested in freezing and thawing conditions according to KTMR-22 (2006) to determine if the freeze-thaw behavior could be improved through these nanotechnologies.

Chapter 2: Materials

Limestone coarse aggregate with poor freeze-thaw durability was treated with various compounds to assess the impact on durability. Three types of metal oxide nanoparticles, three types of sealers, and two latex additives were used in the project testing to enhance the concrete freeze-thaw performance. Nanoparticles were applied using two methods involving vacuum saturation to impregnate the aggregates with the nanoparticles. Aggregates were soaked in the sealers and one of the latex additives for 24 hours and dried prior to batching concrete. The second latex additive was added directly to the concrete to determine if the latex could keep water out of the aggregates by reducing water ingress into the concrete.

2.1 Aggregate

The fine aggregate used was Kansas River sand as specified by the KTMR-22 (2006) test. There were two coarse aggregates used in this study, both used in the K-TRAN: KSU-11-2 study (Riding, Blackwell, Momeni, & McLeod, 2013). Aggregate C from the K-TRAN: KSU-11-2 project was used to assess the first nanoparticle treatment method. This aggregate was from Hunt-Martin Ottawa quarry (4-030-02). The other methods were assessed using Aggregate D aggregate, also from K-TRAN: KSU-11-2. Aggregate D was from the Avoca ledge of the Plummer Creek quarry, quarry number 1-070-11-LS. This ledge was a commercial grade limestone, not a KDOT-approved source for on-grade concrete. Coarse aggregates were rinsed with tap water and oven-dried before applying any treatment methods to remove undesirable fines present on the surface. The aggregate specific gravity and absorption were determined according to KT-6: Procedure I (2011).

The aggregate specific gravity (SG) and absorption values of the fine aggregate (FA) and coarse aggregate (CA) are shown in Table 2.1.

Table 2.1: Aggregate Properties

	Bulk SG	Abs (%)
Fine Aggregate	2.609	0.5
Coarse Aggregate C	2.61	3.0
Coarse Aggregate D	2.51	2.6

2.2 Cement

The cement used for the entire project was a Type I/II cement produced by Monarch Cement. The cement was chosen as specified by the KTMR-22 (2006) test, which requires the cement to meet Type II classification and be produced by Monarch Cement. The composition of the cement used is given in Table 2.2.

Table 2.2: Cement Composition

	Content
SiO ₂ (%)	21.9
Al ₂ O ₃ (%)	4.3
Fe ₂ O ₃ (%)	3.4
CaO (%)	63.7
MgO (%)	2.0
Na ₂ O (%)	0.2
K ₂ O (%)	0.5
Na ₂ O _{eq} (%)	0.5
SO ₃ (%)	2.6
LOI (%)	0.5
Free CaO (%)	0.9
C ₃ S (%)	51.7
C ₂ S (%)	23.8
C ₃ A (%)	5.5
C ₄ AF (%)	10.4

2.3 Nanoparticles

Aggregates were treated with three different nanoparticles: titanium (IV) oxide, magnesium oxide, and aluminum oxide, provided by the NanoScale Corporation. The particles had problems with dispersion and tended to aggregate. Two variations of vacuum saturation were attempted to treat the aggregates, both using a Misonix XL2020 Sonicator to disperse the particles in suspension when impregnating aggregates.

2.4 Sealers

Five sealers were used in this study to treat aggregates for initial water absorption screening tests. Sealer 1 is a waterborn silane-siloxane based sealer intended for use in concrete. Sealer 2 is a silane/siloxane based sealer intended for brick and stone use. Sealer 3 contains 20-45% potassium methyl siliconate and is meant for sealing concrete. Sealer 4 is 90% oxityltriethoxysilane and 1-10% siloxane and silane ester based penetrating sealer. Sealer 5 contains 40% octyltriethoxysilane. Based on the water absorption tests, three sealers were used to treat the coarse aggregates used in concrete samples: Sealers 1, 2, and 3.

The coarse aggregates were immersed in the products as received (no dilution) for 24 hours and dried before batching concrete. The drying period was about 7 days, with an exception. Sealer 1 was given more time based on an interpretation of the instructions on the container. Twenty-one days are referred to for concrete curing and 7 days for curing of the product.

2.5 Latex Additives

Latex A was used to treat coarse aggregates used in concrete samples, while Latex B was used as an additive to concrete to reduce water penetration. With Latex A, the coarse aggregates were immersed in an 8% by weight solution made with distilled water for 24 hours and dried before testing. Latex B was added as a powdered addition to the concrete at a dosage of 1% by weight of cement in one mixture.

2.6 Mixture Proportions

The concrete mixture proportions used in this study are given in Table 2.3. Nanoparticle mixtures were batched with oven-dry coarse aggregate, and the sealer/latex mixes were batched using saturated-surface-dry (SSD) condition coarse aggregate. Air entraining admixture (AEA) dosages were adjusted to give fresh air contents between 5% and 7%, except for Mixture O-2. Mixture O-2 had 7.8%, even though the AEA dosage was 46% less than the Control 2 AEA dosage. It is believed that the air content was higher for Mixture O-2 because the latex admixture entrained air on its own. Mixtures Control 1, T-1, M-1, and A-1 were made with Aggregate C. The remaining aggregate were made with Aggregate D. The latex treated aggregate weights were adjusted slightly because of the effects of the latex treatment on the coarse aggregate SSD specific gravity.

Table 2.3: Theoretical Mixture Design

	Treatment	Cement	Water	Fine Aggregate (SSD)	Coarse Aggregate (SSD)
		lbs/yd ³	lbs/yd ³	lbs/yd ³	lbs/yd ³
Control 1	-	602	235	1506	1506
Control 2	-	602	235	1513	1460
T-1	Titanium Nanoparticles, Treatment 1	602	235	1506	1506
M-1	Magnesium Nanoparticles, Treatment 1	602	235	1506	1506
A-1	Alumina Nanoparticles, Treatment 1	602	235	1506	1506
T-2	Titanium Nanoparticles, Treatment 2	602	235	1513	1460
M-2	Magnesium Nanoparticles, Treatment 2	602	235	1513	1460
A-2	Alumina Nanoparticles, Treatment 2	602	235	1513	1460
S-1	Sealer 1	602	235	1513	1460
S-2	Sealer 2	602	235	1513	1460
S-3	Sealer 3	602	235	1513	1460
O-1	Latex 1, Latex Treatment 1	602	235	1511	1452
O-2	Latex 2, Latex Treatment 2	602	235	1511	1452

Chapter 3: Methods

3.1 Aggregate Treatment Methods

3.1.1 Nanoparticle Treatment Method Number 1

In Treatment Method #1, washed oven-dry coarse aggregates were immersed in a solution of nanoparticles in the bottom half of a vacuum desiccator. An XL2020 Sonicator at power level 6 was used to disperse the particles in a stirring motion for 20 seconds, the tip of the Sonicator kept under the solution level during the process, taking care not to contact the aggregates. The desiccator was evacuated for 5 minutes at 50 ± 3 mm Hg, after which the aggregates were removed. More solution was added to maintain a constant fluid level, though the solution was not changed out. Aggregates weighing 2.5 lbs were treated in approximately 5 lbs of water at a time. Aggregates were then oven-dried at 80°C and cooled to room temperature before batching.

Each nanoparticle solution was made using distilled water and the nanoparticle amount was determined based on the weight of titanium oxide initially used. The titanium nanoparticle solution was initially prepared at a solute to solvent ratio of 1:200 by weight of titanium oxide (1g of titanium oxide to 200g of distilled water). The ratio was doubled to 1:100 by weight of titanium oxide for added solution. The nanoparticles did not stay suspended very well, and even at the dilute ratio the nanoparticles settled out of solution rapidly. The dilution ratios were adjusted for alumina and magnesium nanoparticles based on the molecular weight ratios. For example, to determine the amount of alumina nanoparticles to add, the titanium nanoparticle amount was multiplied by the ratio of the molecular weight of aluminum oxide (Al_2O_3) divided by the molecular weight of titanium (IV) oxide (TiO_2). The same process was used for determination of nanoparticle amounts in Treatment Method #2.

3.1.2 Nanoparticle Treatment Method Number 2

In Treatment Method #2, washed oven-dry coarse aggregates were placed in a vacuum desiccator with two valves, one leading to the vacuum pump and the other to a 5-gallon bucket (elevated above the desiccator) containing nanoparticle solution. The hose connecting the 5-gallon bucket to the desiccator also had two valves: at the base of the bucket and the connection

to the desiccator. The desiccator was evacuated to 50 ± 3 mm Hg for three hours. The hose connecting the bucket was then evacuated for a few seconds by opening the valve connecting it to the desiccator. Nanoparticle solution was then introduced by opening the valve at the base of the bucket in order to maintain the vacuum in the aggregates. Solution was allowed to flow until the aggregates were completely immersed, which required between 5 and 10 minutes. The solution flow was then cut off and the desiccator was held under vacuum for another hour. The aggregates were then removed and the solution poured back into the 5-gallon bucket. Aggregates were then oven-dried at 80°C , then cooled to room temperature before batching concrete. Nine pounds of aggregates were treated at a time.

For the nanoparticle solution used in Method #2, the solute to solvent ratio was 1:100 by weight of titanium oxide in both the original solution and added solution. One pound of additional solution was added to the 5-gallon bucket after treating a batch of aggregate. Just before the solution was introduced to the desiccator, the solution was stirred until the nanoparticles were dispersed (about 10-30 seconds, scrapping the bottom of the bucket as well). Then the XL2020 Sonicator was used, again at power level 6, to stir up the particles for 20 seconds. The solution was then introduced into the desiccator. The nanoparticles had trouble staying in suspension very well, and over the course of the hour settled. The alumina nanoparticles particularly did not stay in suspension well and settled out even while solution was still flowing into the desiccator.

3.1.3 Sealer Treatment

Sealer treatment of coarse aggregate consisted of 24 hours immersion in a sealer, followed by a drying period in the laboratory. During the first 24 to 48 hours of the drying period, the aggregates were kept under a fume hood. Aggregates were immersed in a 5-gallon bucket containing the undiluted solution, treating 12-13 lbs of aggregates per treatment. The solution was not changed out, so the same solution was used to treat all the coarse aggregate for one concrete batch, or about 50 lbs. After the drying period, aggregates were immersed in water for 24 hours and towel-dried to a saturated-surface-dry (SSD) condition, then used to batch concrete. The total length of the drying period was 21 days for Sealer 1 and 7 days for Sealer 2 and 3.

3.1.4 Latex Treatment

Two methods of latex treatment were used. In Method #1, the latex compound was diluted in distilled water to form an 8% solution by weight. This was used similarly to the sealers, as the aggregates were immersed in the latex solution for 24 hours followed by a drying period. This method caused the aggregates to stick together, which did not happen for the sealers. After immersion in the solution, the aggregates were spread out over a large clean and dry plastic container lid for the first 48 hours. The total drying period was 6 days. After the drying period, the aggregates were immersed in water for 24 hours and towel-dried to a saturated-surface-dry condition for use in the concrete mixture. In Method #2, powdered latex was used. The latex was added as an admixture in the concrete mix.

3.2 Concrete Mixing Procedures

Concrete mixtures were made according to ASTM Standard C192 (2006). The coarse aggregates that were treated were added to the concrete in their final treated state instead of in the SSD condition to preserve the benefits of the treatments in reducing water adsorption.

3.3 Aggregate Sealer Test

A screening test of the sealers was conducted to determine which three sealers would be used in concrete batching. Washed, oven-dry aggregate was immersed in the sealers for 24 hours and let dry for seven days. The aggregate was then placed in a wire basket and the submerged weight in water recorded over time using a computer to record balance readings. Figure 4.1 shows the submerged weight over time for the various sealers.

3.4 Compressive Strength

Cylinders measuring 4x8 inches were cured for 28 days before compressive strength testing according to ASTM Standard C39 (2014). The cylinders were de-molded 24±4 hours after batching. After de-molding, specimens were stored during the curing period in a 100% moist room at 72°F.

3.5 Freeze-Thaw Testing

The freeze-thaw prisms were cured according to KTMR-22 (2006). The 3x4x16 inch prisms were de-molded after 24±4 hours, then stored in a fog room until 67 days after batching. The prisms were then held in an environmental chamber at 73°F and 50% relative humidity (RH) for 21 days. The prisms were then immersed in room-temperature water for 24 hours, then immersed in water at 40°F for 24 hours, and then subjected to the freeze-thaw test. Samples were then tested for 600 freeze-thaw cycles, or until the relative modulus decreased to below 60%. Freeze thaw testing was conducted in a Scientemp 20 block freeze-thaw chamber. The chamber was set to run eight freeze-thaw cycles per day. Relative modulus and length change measurements were taken as specified in KTMR-22.

Chapter 4: Results

4.1 Sealer Treatment Aggregate Water Uptake

Figure 4.1 shows the sealer treatment aggregate water uptake data. Figure 4.2 shows the aggregate water uptake data as a percent of the initial submerged weight for better comparative purposes. The submerged weight values showed that Sealers 1, 2, and 3 had the slowest water uptake and were used in the concrete freeze-thaw testing. There was a slight decrease in the sample mass for Sealer 5. This was because of experimental error with the measurements, and does not indicate that the sample lost weight for that measurement. Sample mass values before and after sealer treatment are shown in Table 4.1.

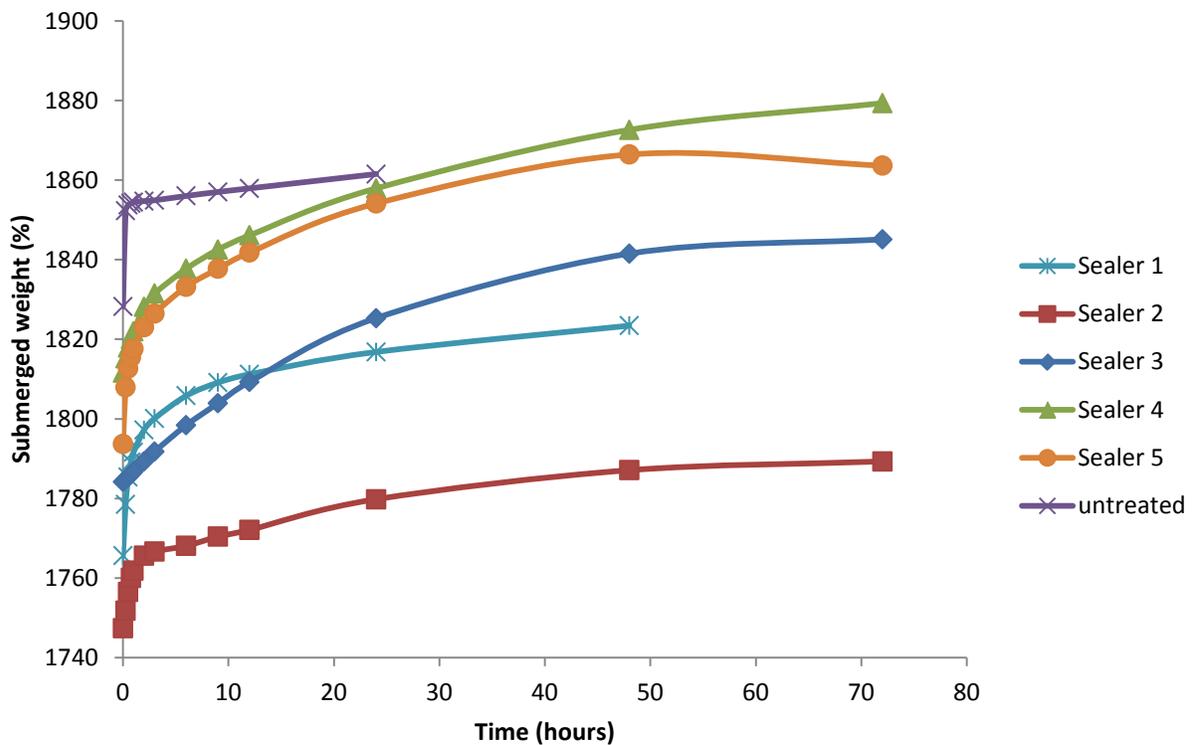


Figure 4.1: Submerged Weight of Aggregate Over Time

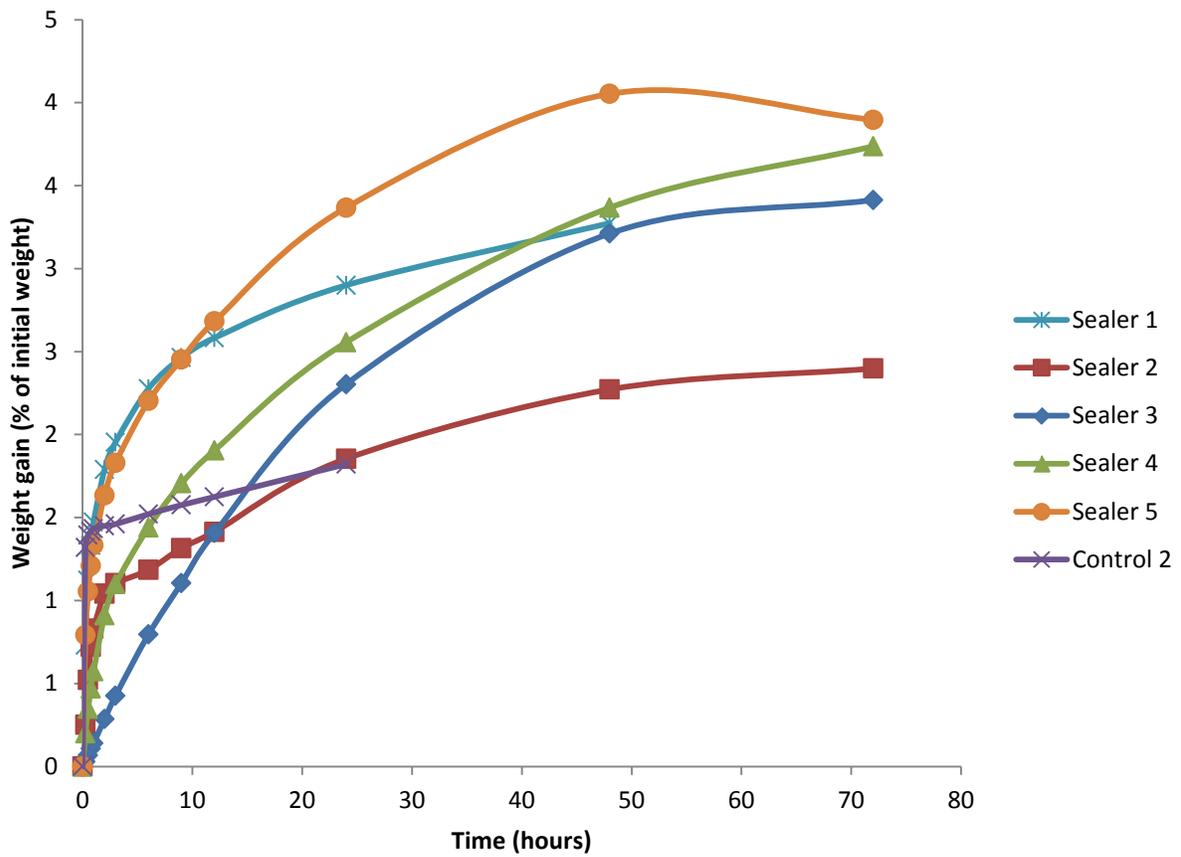


Figure 4.2: Aggregate Percent Weight Change With Time Soaking

Table 4.1: Aggregate Mass Gain After Sealer Treatment

Sealer	Oven Dry Mass (g)	
	Untreated	Treated
Control 2	2959.7	-
Sealer 1	2963.9	2972.1
Sealer 2	2919	2929.7
Sealer 3	2959.7	2973.8
Sealer 4	2969.5	-
Sealer 5	2952.7	2977.6

4.2 Concrete Strength Results

Compressive strength data for the concrete mixtures is shown in Figure 4.3. Mixtures A-2 and S-3 were particularly weak. S-1, S-2, and O-1 treatment methods increased 28-day strength, though the cylinders seemed abnormally fragile when de-molded, indicating potentially low early-age strength that recovered before 28 days.

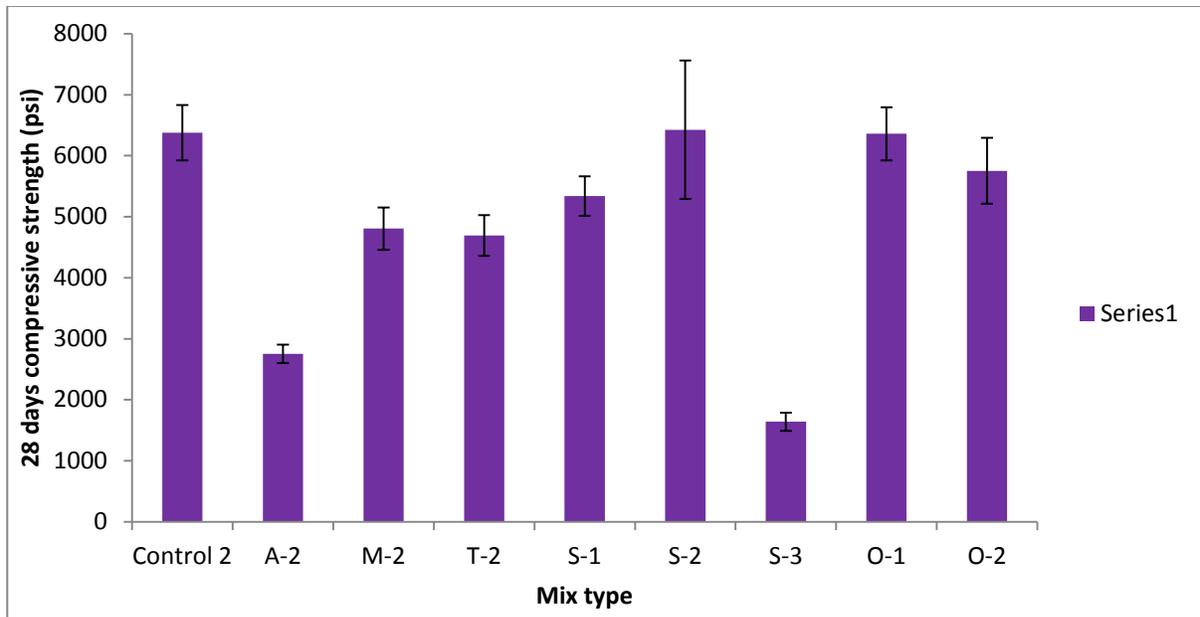


Figure 4.3: Concrete Mixture Average 28-Day Compressive Strength

4.3 Freeze-Thaw Test Results

Average relative modulus data is shown in Figure 4.4 for concrete beams made with Aggregate C and Figure 4.5 for concrete beams made with Aggregate D. Average expansion values for the freeze-thaw prisms are shown in Figure 4.6 for concrete beams made with Aggregate C and in Figure 4.7 for Aggregate D.

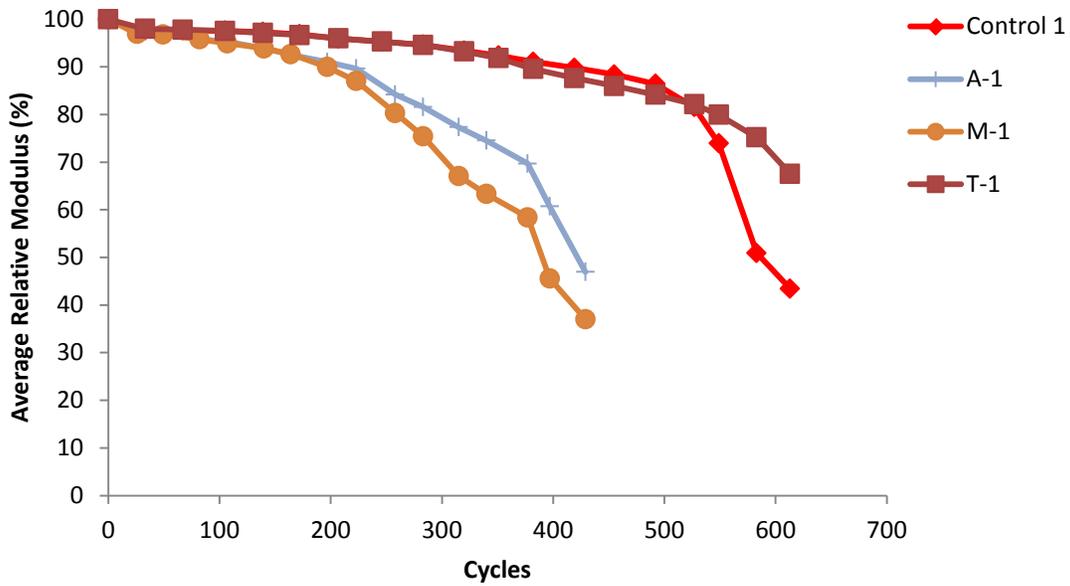


Figure 4.4: Average Relative Modulus vs. Freeze-Thaw Cycles for Concrete Mixtures Made with Aggregate C

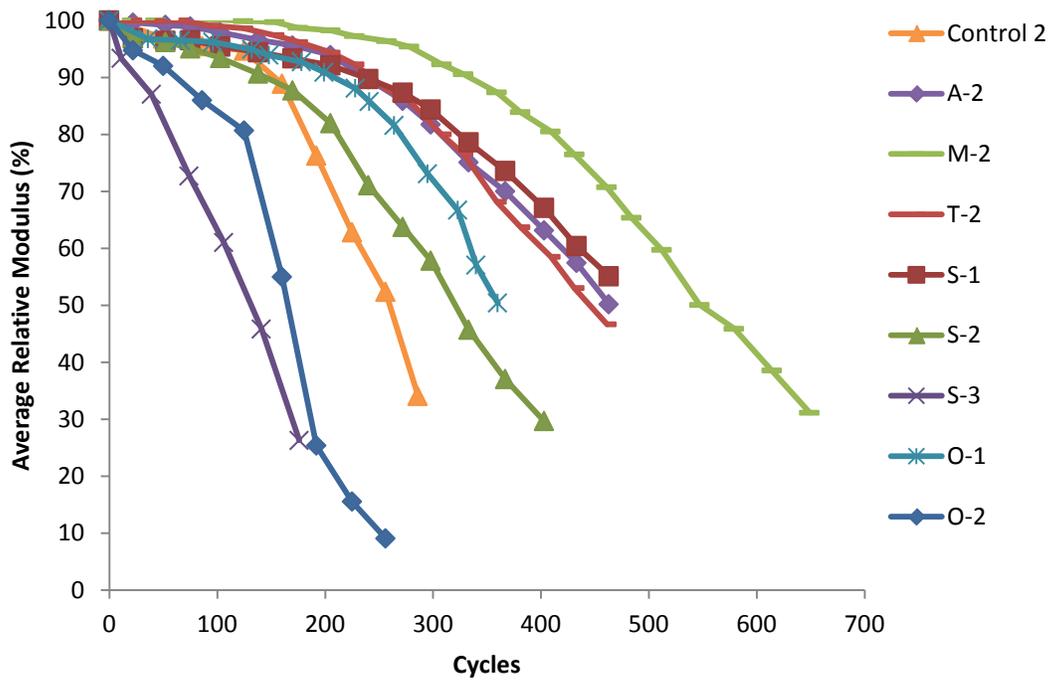


Figure 4.5: Average Relative Modulus vs. Freeze-Thaw Cycles for Concrete Mixtures Made with Aggregate D

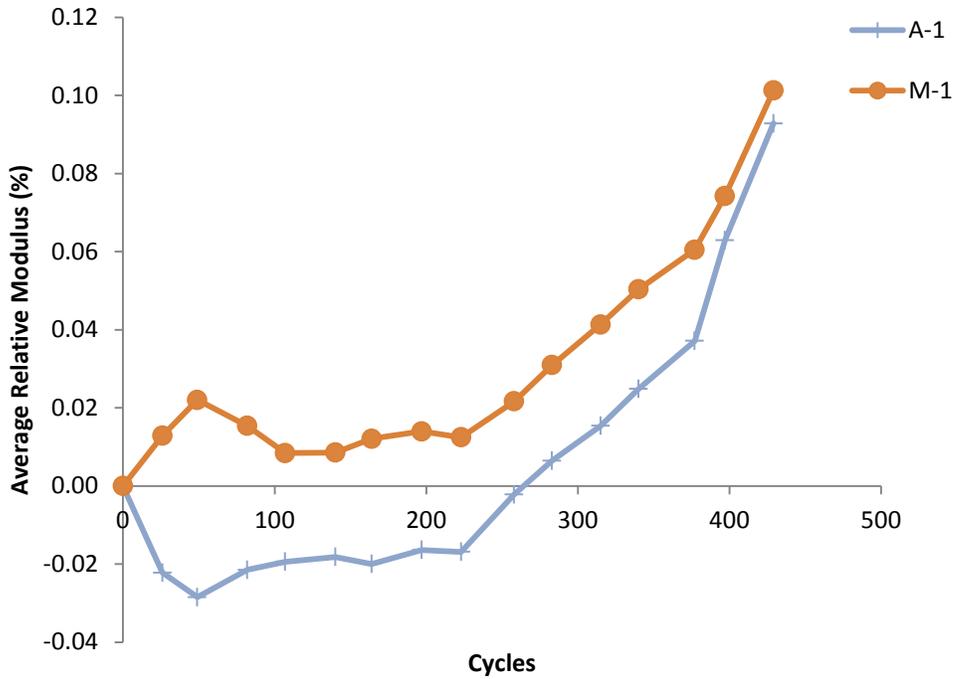


Figure 4.6: Average Concrete Beam Length Change vs. Freeze-Thaw Cycles for Concrete Mixtures Made with Aggregate C

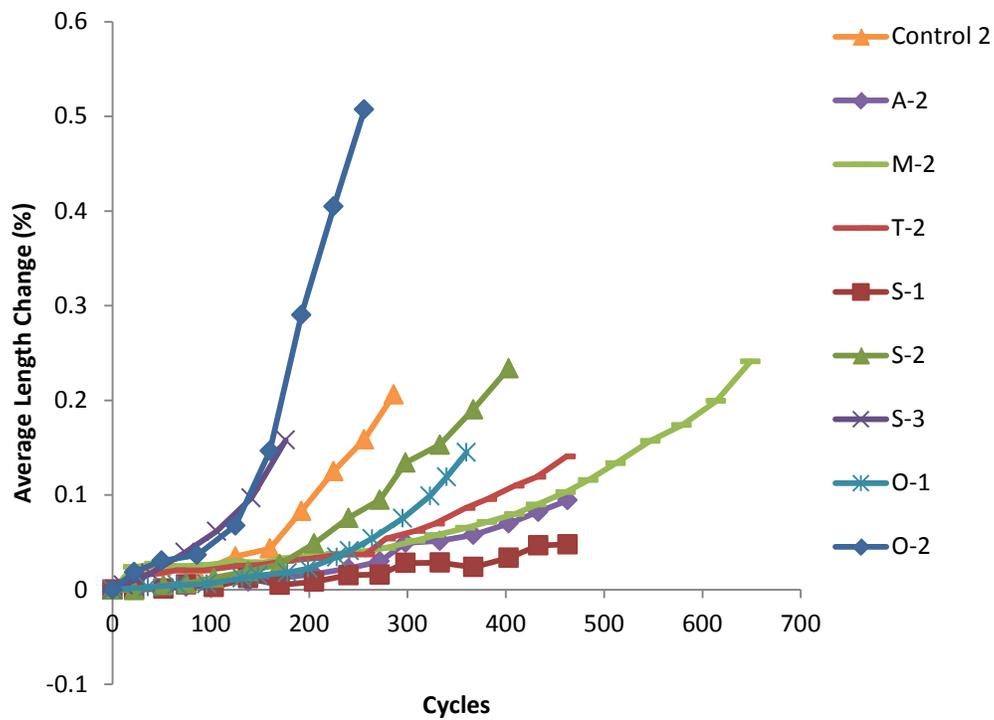


Figure 4.7: Average Concrete Beam Length Change vs. Freeze-Thaw Cycles for Concrete Mixtures Made with Aggregate D

4.3.1 Nanoparticle Results

Frost durability was not improved significantly by nanoparticle Treatment Method 1, regardless of nanoparticle type. This is most likely because Treatment 1 did a poor job of impregnating the aggregates with the nanoparticles, only depositing on the surface. For about 60 cycles the freeze-thaw chamber only reached a minimum temperature of approximately 10-12°F rather than 0°F. This affected mixes A-1 and M-1 during cycles 315-377. The relative modulus of these mixes continued to decrease with time, and the prisms did not last long enough to run additional cycles to make up for the shortfall. Because of this, the performance of A-1 and M-1 is suspect, and the mixes are even less durable than is indicated in the figures. Indeed, roughly for cycles 315-377 for M-1 and A-1, the slope of the relative modulus line is slightly decreased then increases again after the chamber was repaired, indicating that damage was reduced for these cycles. There were problems with the expansion measurements for the control and T-1 samples; however, the relative modulus values confirmed the poor performance of these aggregates.

The concrete made with aggregates treated by nanoparticle Treatment 2 showed some marginal improvements over the control concrete mixture. The low compressive strength of Mixture A-2 did not seem to have been a factor in reducing the performance of the concrete mixture, though it might be with less curing time.

4.3.2 Sealer Results

Sealer treatment was mixed in performance. Concrete Sealers 1 and 2 provided some minor benefits to the aggregate freeze-thaw performance; however, Sealer 3 decreased the freeze-thaw performance. The very low compressive strength of S-3 may have been a factor. Additionally, it is possible the potassium methyl silicate used in Sealer 3 made it difficult for water that did adsorb into the aggregate to escape the aggregate during a freezing event.

4.3.3 Latex Results

Treatment of aggregate with latex compound using Method #1 (O-1) very slightly improved the freeze-thaw durability of the aggregate. However, adding latex compound as powder in the mix (O-2) reduced freeze-thaw performance of concrete, as shown in Figure 4.5 and Figure 4.7. This could be because the latex additive added to the concrete made it difficult

for water that did adsorb into the concrete from escaping into the air voids in the paste during a freezing event, causing it to freeze in the aggregate pores. The latex additive, when applied to the aggregate, may have blocked some pores for water absorption, but not affected the permeability of the paste, which would make it more difficult for the water that did make it into the aggregate to escape during freezing.

Chapter 5: Conclusions and Recommendations

Nanotechnology was used to treat limestone aggregates with a poor freeze-thaw performance record in concrete to determine if they could improve the concrete performance in freeze-thaw tests. Silica, alumina, and titanium nanoparticles, three different types of sealers, and two latex additives were used to treat the aggregates and concrete mixtures. The use of vacuum impregnation with nanoparticles was found to only slightly improve the performance of poor freeze-thaw durable aggregates. The use of the silane/siloxane based sealers was found to slightly improve the performance of the aggregates, whereas the use of the potassium methyl silicate sealer did not. When added to the concrete as a powdered additive, latex additives were found to increase the rate of freeze-thaw damage of concrete containing poor-quality aggregates. None of the treatments used were able to improve the performance of the aggregates enough to make them usable in Kansas concrete pavements. Future research could focus on the use of superhydrophobic emulsions that could help keep the water out of the concrete and prevent the aggregates from becoming saturated.

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