UNIVERSITY OF UND NORTH DAKOTA

September 27, 2013

Karlene Fine, Executive Director
North Dakota Industrial Commission
State Capitol – 14th Floor
600 East Boulevard Ave Dept 405
Bismarck, ND 58505-0840

DEPARTMENT OF CIVIL ENGINEERING
UPSON II ROOM 260
243 CENTENNIAL DRIVE STOP 8115
GRAND FORKS ND 58202-8115
PHONE (701) 777-3562 /FAX (701) 777-3782
www.civilengineering.und.edu/

Dear Ms. Fine:

Please find enclosed here in the proposal titled, Investigating the Use of Fly Ash and Nanomaterials for Sustainable Concrete Infrastructure.

The main criteria for a sustainable infrastructure are: minimizing impact on and the use of natural resources; reducing energy consumption; reducing greenhouse gas emissions; limiting pollution (air, water, earth, noise); improving health, safety, and risk prevention; and ensuring a high level of user comfort and safety. The potential effect of nanomaterials on concrete infrastructure in terms of sustainability lies in the efficient use of existing materials either through reworking them and changing their structures to ensuring that the properties of the materials are improved to provide a longer life. Use of fly ash in concrete helps to reduce cost, conserve energy and resources, reduce environmental impact, and enhance workability. The main objective of this project is to test the hypothesis that ordinary Portland cement can be fully replaced by fly ash and nanomaterials in concrete since nanomaterials can accelerate the rate of hydration reaction of fly ash in concrete and improve its desirable properties.

The research team has the experience and expertise to complete the research within the schedule and budget. The University of North Dakota is committed to complete the project as described in the application if the North Dakota Industrial Commission makes the grant requested.

We welcome an opportunity to discuss this proposal at greater length with you and look forward to working with you.

Sincerely,

Barry Milavetz, Ph.D.
UND Associate Vice President for Research
Office: 701- 777-4278
E-mail: barry.milavetz@email.und.edu

Daba S. Gedafa, Ph.D., P.E.,
Principal Investigator
Office: 701-777-3979
Email: daba.gedafa@engr.und.edu

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# Investigating the Use of Fly Ash and Nanomaterials for Sustainable Concrete Infrastructure

Applicant and Principal Investigator:

Daba S. Gedafa, Ph.D., P.E.
Assistant Professor
UND Civil Engineering
Upson II Room 260K
243 Centennial Dr. Stop 8115
Grand Forks, ND 58202-8115
Tel. (701) 777-3976
E-mail: daba.gedafa@engr.und.edu

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# TABLE OF CONTENTS

# ABSTRACT

The main criteria for a sustainable infrastructure are: minimizing impact on and the use of natural resources; reducing energy consumption; reducing greenhouse gas emissions; limiting pollution (air, water, earth, noise); improving health, safety, and risk prevention; and ensuring a high level of user comfort and safety. The potential effect of nanomaterials on concrete infrastructure in terms of sustainability lies in the efficient use of existing materials either through reworking them and changing their structures to ensuring that the properties of the materials are improved to provide a longer life. Use of fly ash in concrete helps to reduce cost, conserve energy and resources, improve durability, reduce environmental impact, and enhance workability. The main objective of this project is to test the hypothesis that ordinary Portland cement can be fully replaced by fly ash and nanomaterials in concrete since nanomaterials can accelerate the rate of hydration reaction of fly ash in concrete and improve its desirable properties. The research team anticipates that the use of fly ash and nanomaterials in concrete will improve workability; reduce water demand, corrosion of reinforcing steel, segregation, bleeding, heat evolution, and permeability; inhibit alkali-aggregate reaction; and enhance sulfate resistance in addition to economic and ecological benefits. The project will be for duration of one year. The total project cost is 60,642. The participants with percent cost in parenthesis are: North Dakota Industrial Commission (24%), Great River Energy (25%), and Civil Engineering Department at the University of North Dakota (51%).

## PROJECT SUMMARY

The main criteria for a sustainable infrastructure are: minimizing impact on and the use of natural resources; reducing energy consumption; reducing greenhouse gas emissions; limiting pollution (air, water, earth, noise); improving health, safety, and risk prevention; and ensuring a high level of user comfort and safety. The potential effect of nanomaterials on concrete infrastructure in terms of sustainability lies in the efficient use of existing materials either through reworking them and changing their structures to ensuring that the properties of the materials are improved to provide a longer life.

Use of fly ash in concrete helps to reduce cost, conserve energy and resources, reduce environmental impact, enhance workability, and improve durability. The main objective of this project is to test the hypothesis that ordinary Portland cement can be *fully replaced by fly ash and nanomaterials in concrete* since nanomaterials can accelerate the rate of hydration reaction of fly ash in concrete and improve its desirable properties. Fly ash from coal creek station and four different types of nanomaterials will be used. The four nanomaterials are: nano alumina, nano silica, nano silica wire, and nano clay. Nanomaterial percent (by weight) will be increased starting at 0.5%, by 0.5% until properties equivalent/better as compared to the ordinary Portland cement-based concrete (control) are achieved. Fresh and hardened properties of concrete will be considered in addition to durability. Fresh properties include: slump test, unit weight, and air content. Hardened properties include: compressive strength, flexural strength, tensile strength, and modulus of elasticity. Hardened properties will be determined using Universal Testing Machine. Nanostructural morphology and elemental compositions will also be investigated using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Statistical analysis (analysis of variance and t-test) will be conducted at 5% significance level to determine equivalency between the control and fly ash-based concrete.

# 1. PROJECT DESCRIPTION

## 1.1 Objectives

The main criteria for a sustainable infrastructure are: minimizing impact on and the use of natural resources; reducing energy consumption; reducing greenhouse gas emissions; limiting pollution (air, water, earth, noise); improving health, safety, and risk prevention; and ensuring a high level of user comfort and safety *(Maher et al. 2006)*. The potential effect of nanomaterials on concrete infrastructure in terms of sustainability lies in the efficient use of existing materials either through reworking them and changing their structures to ensuring that the properties of the materials are improved to provide a longer life *(Cassar 2005)*.

The main objective of this project is to test the hypothesis that ordinary Portland cement can be *fully replaced by fly ash and nanomaterials* in concrete since nanomaterials can accelerate the rate of hydration reaction of fly ash in concrete and improve its desirable properties. There will be four specific objectives in this project:

- To determine fresh properties of fly ash and nanomaterials-based concrete and the control
- To determine the mechanical properties of fly ash and nanomaterials-based concrete and the control
- To measure nanostructural properties of fly ash and nanomaterials-based concrete and the control
- To investigate freeze-thaw resistance of fly ash and nanomaterials-based concrete and the control

## 1.2 Methodology

### 1.2.1 Selection of Nanomaterials

Due to exponential growth of population and availability of limited natural resources, extensive scientific explorations have been carried out to identify additional available raw materials that can be engineered and utilized. It has been found that the most available raw minerals, such as clay and silica, have huge potential for use in the construction industry.

Nano alumina can be used as a reactive agent to increase the hydraulic activity of slowly reactive materials such as fly ash and to refine the microstructure of paste, leading to the improvement of mechanical strength at early ages *(Campillo et al. 2007)*.

Colloidal nanomaterials performed better than powder forms. This behavior was partially attributed to the smaller particle size of the former because the inclusion of stabilizers in their formulation prevents agglomeration. Furthermore, dispersion of nanomaterials within the paste was more effective for colloidal dispersions, resulting in pastes that were more homogeneous and that had smaller porosity (*Campillo et al. 2007, Gaitero et al., 2010, Porro et al. 2010*).

Four different colloidal nanomaterials have been selected for use in this project based upon their performance and availability. Availability is important for large concrete infrastructure projects. These nanomaterials include: Nano alumina, Nano silica, Nano silica wire (NSW), and Nano clay. NSW has never been used in concrete. The research team believes that the wires will act as reinforcement in fly ash-based concrete.

### 1.2.2 Experimental Plan

Nanomaterial type, nanomaterial contents, and curing period will be considered as variables. Primary nanomaterials and secondary nanomaterials combination groups will be considered. At least five specimens will be tested in each test category so that enough data will be available for statistical analysis. Table 1 shows the types of tests to determine mechanical, nanomechanical, and resistance to freeze-thaw properties. All the tests have the same curing period except compressive strength.

**Table 1. Properties, Curing Period, and Equipment**

| Property | | Curing Period (days) | Equipment |
|---|---|---|---|
| Nanostructural morphology and elemental composition | | 3,7,14,28 | SEM/EDS |
| Mechanical properties | Compressive strength | 3,7,14,28,90 | Universal Testing Machine |
| | Flexural strength | 3,7,14,28 | |
| | Tensile strength | | |
| | Modulus of elasticity | | |
| Freeze-thaw resistance | Durability | | Rapid Freeze-thaw Cabinet |

For comparison purposes, the primary experimental plan for the tests will include preparing and testing five broad concrete test categories in primary combination groups: (1) Ordinary Portland cement-based concrete (control), (2) Fly ash and Nano alumina-based concrete, (3) fly ash and Nano silica-based concrete, (4) fly ash and Nano silica wire-based concrete, and (5) fly ash and Nano clay-based concrete. Nanomaterial percent (by weight) will be increased starting at 0.5%, by 0.5% until optimum content is achieved or properties equivalent/better as compared to the control are achieved. Studies have shown different optimum amounts of nanomaterials that produce optimum mechanical properties in ordinary Portland cement mortar and concrete *(Chang et al. 2007, Givi et al. 2010, Mondal et al. 2010, Nazari and Riahi 2011)*.

In addition to the primary group combinations, a secondary experimental plan will be used to investigate the effect of combinations of nanomaterials on fly ash-based concrete properties. Secondary combination will result in six different categories. Each nanomaterials type will be increased at 0.5%. The properties from secondary combination will be compared to the control and primary combination having the same amount of nanomaterials.

#### 1.2.2.1 Mixing

Effective dispersion of nanomaterials is critical to achieving the full benefits in cementitious system. Self-aggregation, especially at high dosages of nanomaterials, is a common concern *(Qing et al. 2006, Sobolev et al. 2006, Veras-Agulho et al. 2009, Ozyildirim and Zegetosky 2010, Sanchez and Sobolev 2010*), which sometimes leads to nonhomogeneous microstructure development and poor performance. The application of super-plasticizer and high-speed mixing were found to be effective in proper dispersion of nanomaterials *(Sobolev et al. 2006, Flores et al., 2010).* Colloidal nanomaterials will be mixed with a super-plasticizer at high-speed in this project.

#### 1.2.2.2 Fresh Properties

Fresh property tests will include: unit weight, air content, slump, and temperature. The loss of air content from fresh concretes is increased with a higher content of nanomaterials. However, the required concrete air content can be achieved by increasing the dosage of air entraining admixture *(Gonzalez et al. 2013).* Air entraining admixture will be added in order to achieve the required air content for durability of concrete. Pressure method will be used to measure air content following American Society for Testing Materials (ASTM) standard (ASTM C231M). The density of fresh concrete will be measured following ASTM C138M.

The introduction of nanomaterials in concrete results in a workability loss in the mix due to high specific surface area of the nanomaterials *(Bjornstrom et al. 2004, Hiisken and Brouwers 2008, Hosseini et al. 2009, Senff et al. 2010, Nazari and Riahi 2011, Gonzalez et al. 2013).* Super-plasticizers will be added to improve the workability of the specimens. Slump will be measured according to ASTM C143M.

### 1.2.2.3 Mechanical Properties

This will identify whether or not the mechanical properties of fly ash and nanomaterials-based concrete can be equivalent to or better than those of ordinary Portland cement-based concrete. Mechanical properties of fly ash and nanomaterials-based concrete will be measured using a Universal Testing Machine (UTM). Mechanical properties include: compressive strength, flexural strength, tensile strength, and modulus of elasticity.

***Compressive Strength:*** Concrete is normally capable of developing significant compressive strength. Compressive strength is used to design structural elements in civil infrastructure. Addition of nanomaterialss improves the compressive strength of ordinary Portland cement mortar and concrete *(Sobolev et al. 2006, Chang et al. 2007, Gaitero et al. 2008, Sobolev et al. 2008, Gaitero et al. 2009, , Morsy et al. 2009, Sobolev et al. 2009, Flores et al. 2010, Gaitero et al. 2010, Nazari and Riahi 2012, Gonzalez et al. 2013).* In another study, addition of Nano alumina has had a limited effect on the compressive strength of concrete *(Li et al. 2006)*.

The compressive strength of concrete specimens will be tested using Universal Testing Machine after proper curing according to ASTM C39M.

***Flexural Strength:*** Flexural strength, also known as modulus of rupture, bend strength, or fracture strength, is a critical mechanical property for brittle material, and is defined as a material's ability to resist deformation under load. It is mostly used for the design of concrete pavements. Research showed that the flexural strengths of cement mortars containing Nano silica increases *(Li et al. 2004, Sobolev et al. 2009, Flores et al. 2010).* ASTM 348-08 will be followed to test concrete beam specimens for flexural strength using Universal Testing Machine.

***Tensile Strength:*** Tensile strength of concrete is only a fraction of its compressive strength. Increased tensile strength allows greater bending before rupture and can minimize the shrinkage cracking potential of concrete. The ability to be more ductile would allow designers to reduce the thickness of pavements and, possibly, of bridge decks. Designers could greatly increase the spacing of joints or eliminate them altogether. Both structures and pavements would possess increased ability to withstand dynamic loadings, which would prolong useful life *(Metaxa et al. 2009)*.

Incorporation of Nano clay was reported to enhance the tensile strength in a cement composite *( Morsy et al. 2010)*. The effect of fly ash and nanomaterials-based concrete will be investigated using a split test method with Universal Testing Machine according to ASTM C496M-11.

***Modulus of Elasticity and Poisson's Ratio:*** *Kim et al. (2010)* and *Li et al. (2006)* reported an increase in modulus of elasticity of ordinary Portland cement-based concrete due to addition of Nano silica and Nano alumina, respectively. Stress and strain will be measured using Universal Testing Machine according to ASTM C469M-10 and will be used to calculate the modulus of elasticity of concrete. Poisson's ratio will be calculated as the ratio of measured transverse and axial strains.

### 1.2.2.4 Nanostructural Morphology and Elemental Composition

The Nano-fiber nature of Nano clay and their filler effect in cement mortar was revealed by morphological studies using scanning electron microscopy (SEM). The texture of hydrate products was found to be denser, compact, and with uniform microstructure. SEM tests indicated that the specific surface area of Nano clay is the key factor for denser microstructure of samples *(He and Shi 2008, Morsy et al 2009*). SEM tests revealed that the micro-structure of Nano silica concrete is more uniform and compact than of normal concrete, with stronger bond between the cement matrix and aggregates due to reaction with $Ca(OH)_2$ crystals and reduction of their size and amount *(Scrivener et al. 2004, Elsharief et al. 2005, Li et al. 2004, Ji 2005, Qing et al. 2007).*

Nanostructural morphology and elemental composition analysis of fly ash and nanomaterials-based concrete will be conducted using SEM and energy dispersive spectroscopy (EDS).

***Preliminary Data:*** Ordinary Portland cement-based concrete specimen (40 mm diameter and 35 mm height) was prepared and cured for 7-days. SEM (Hitachi S-3400N) was used to determine the microstructural morphology of the specimen as shown in Figure 1. The same equipment will be used to determine the morphology of fly ash and nanomaterials-based concrete and compare it to the control (ordinary Portland cement-based concrete) in this project.

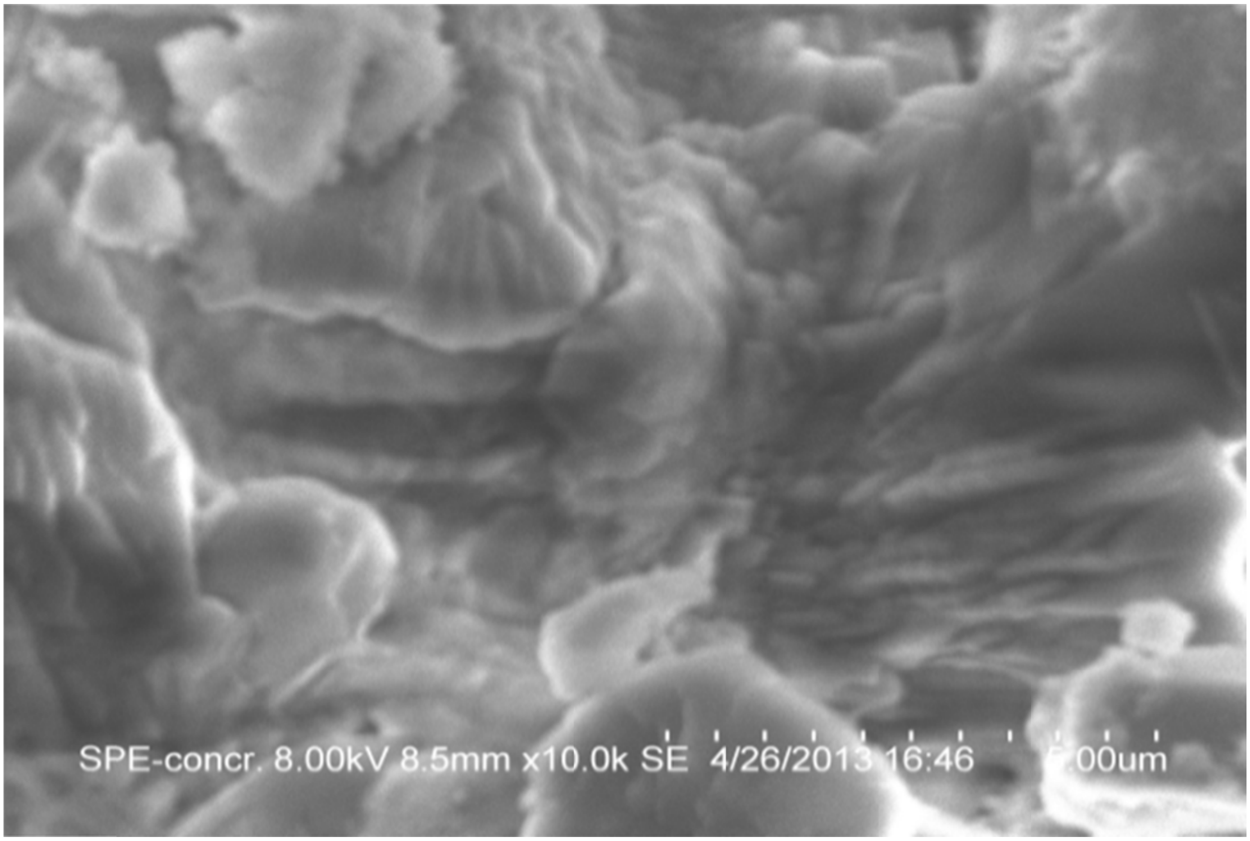

Figure 1. Microstrucure of concrete specimen.

Elemental composition analysis will help determine the type of element responsible for certain types of concrete properties. Elemental composition of the same concrete specimen was analyzed using EDS. Figure 2 shows elemental composition of the specimen. Table 2 shows summary of elemental composition in terms of percent concentration and atomic for each element. Oxygen and iodine shows the highest and lowest percent concentration and atomic, respectively.

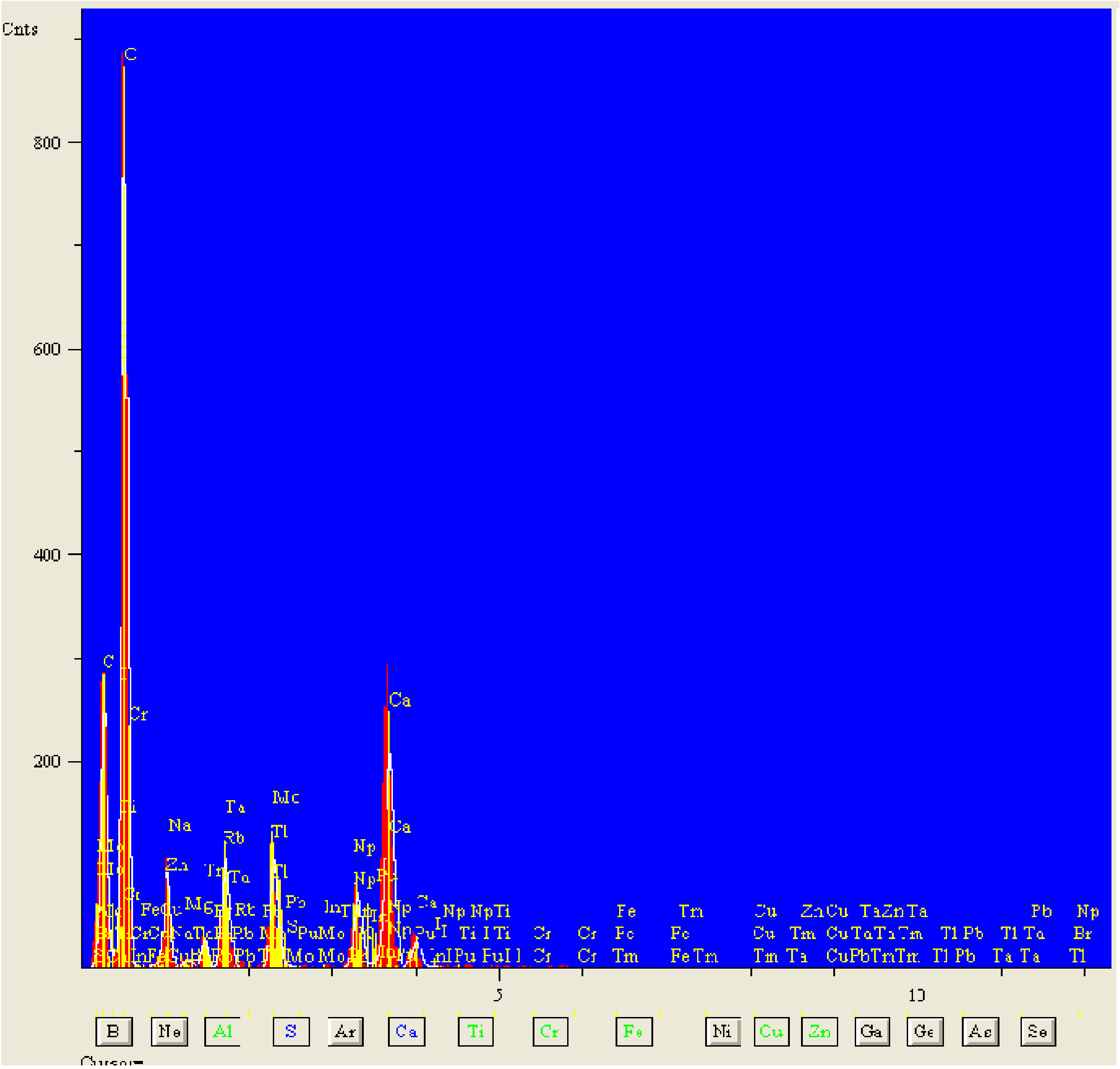

Figure 2. Elemental composition using EDS.

Table 2. Elemental composition of concrete specimen

| | Oxygen | Calcium | Carbon | Potassium | Sulfur | Indium | Iodine | Others |
|---|---|---|---|---|---|---|---|---|
| Concentration (wt.%) | 45.978 | 21.666 | 15.963 | 4.813 | 4.102 | 2.994 | 1.979 | 2.505 |
| Atomic (%) | 56.184 | 10.569 | 25.984 | 2.406 | 2.501 | 0.51 | 0.305 | 1.541 |

### 1.2.2.5 Freeze-Thaw Resistance

A durable transportation infrastructure needs to satisfy two requirements: service with a minimum requirement for maintenance and sustainability. The durability requirement focuses on the potential perpetual use of the facility with minimum requirement for disruptive maintenance and rehabilitation *(Li et al. 2006)*. All failure mechanisms associated with concrete durability involve transportation of fluids through the concrete microstructure. The movement of water into and through concrete can contribute to many of the deterioration mechanisms that affect concrete performance. Water itself can result in freeze–thaw damage if a proper air-entraining system is not in place. In northern climates such as North Dakota, deicing chemicals can adversely affect longevity if the concrete properties are marginal or inadequate. Nanomaterials could greatly increase the life of concrete structures if a method could be developed to make concrete less permeable. This may pave the way to making concrete freeze–thaw resistant without air entraining *(Grove et al. 2010)*.

Addition of nanomaterials increase durability and service life of concrete by reducing permeability to fluids and by controlling the leaching of calcium *(Kroyer et al. 2003, Ji 2005, Sobolev 2005, Cardenas et al.2006, Gaitero et al. 2006, Gaitero et al. 2008, He and Shi 2008, Gaitero et al. 2010, Porro et al. 2010, Nazari and Riahi 2011, Zhang and Li 2011, Nazari and Riahi 2012, Zhang and Wang 2013)*.

One of the problems with using fly ash in concrete is an increased potential for frost damage *(Taylor et al. 2007)*. The Rapid Freeze-Thaw Cabinet will be used to measure the resistance of fly ash and nanomaterials-based concrete and ordinary Portland cement-based concrete to deterioration caused by repeated cycles of freezing and thawing.

#### 1.2.2.5 Statistical Analysis

Paired t-tests will be performed to evaluate if there is a significant difference between the properties of fly ash and nanomaterials-based concrete in primary and secondary combinations and ordinary Portland cement-based concrete properties *(SAS Institute, Inc. 2005).* A paired t-test result can be expressed in terms of a p-value, which represents the weight of evidence for rejecting the null hypothesis (*Ott and Longnecker 2001).* Significance level of 5% will be used for all paired t-tests. Analysis of variance (ANOVA) will also be conducted at the same significance level using Statistical Analysis Software (SAS).

## 1.3 Anticipated Results

Fly ash has many of the chemical properties of ordinary Portland cement. It includes constituents such as silica, alumina, iron, and other oxides. These characteristics allow fly ash to replace Portland cement in concrete products.

The research team anticipates that the use of fly ash and nanomaterials in concrete will improve workability; reduce water demand, corrosion of reinforcing steel, segregation, bleeding, heat evolution, and permeability; inhibit alkali-aggregate reaction; and enhance sulfate resistance in addition to in addition to economic and ecological benefits.

## 1.4 Facilities and Resources

### 1.4.1 Material Testing Laboratory and Equipment

The Department of Civil Engineering at the University of North Dakota owns a 625 square meter of research laboratory dedicated to civil engineering materials testing in Upson I Rooms 112 and 113. The laboratory is fully equipped with state-of-the-art facilities that will used to test civil engineering materials. The equipments needed for this project are described below.

**Aggregate Testing**: The research team has all the equipment needed for sieve analysis, specific gravity, bulk density, moisture content, and absorption of aggregates.

**Mixing**: The research team has two high-speed mixers.

**Fresh Property**: The research team has a measure to determine density, air meter to determine air content using pressure method, and slump cones to determine slump of fresh concrete.

**Curing:** The research team has a large moist curing room (5 m by 5 m) with temperature and moisture control. There are three layers of shelves on the three sides of the room.

**Mechanical Property**: The research team has a Universal Testing Machine (13,335 kN capacity) to determine compressive strength, flexural strength, tensile strength, and modulus of elasticity of hardened concrete specimens. All the accessories needed for all the tests are also available.

**Nanostructural Morphology and Elemental Composition Analysis**: The research team has access to SEM and EDS to determine nanostructural morphology and elemental composition analysis.

**Durability Test:** Civil Engineering Department at the University of North Dakota will purchase new Rapid Freeze-Thaw Cabinet to determine the resistance of concrete to deterioration caused by repeated cycles of freezing and thawing in water.

### 1.4.2 Human Resource and Facilities

One quarter time graduate research assistant will work on this project under the guidance of the Principal Investigate (PI), Dr. Gedafa. Administrative assistant will help with payroll, hiring of students, ordering equipment and supplies.

The PI has 4 m by 4 m office space with personal computer and high speed internet access in Upson II Room 260K, which is adjacent to Upson I where laboratory is located. Graduate research assistant has office space in Upson I and personal computer with high speed internet connection. All the computers have the programs and softwares that are needed for this project.

### 1.4.3 Library

The University of North Dakota (UND) has seven different libraries. Chester Fritz Library is the largest library in the university and the state of North Dakota. It houses over two million print and non-print items. It is designated as U.S. Patent and Trademark depository of Federal and State documents. The library also houses a Special Collections Department preserving unique publications, manuscripts, historical records, and genealogical resources. The research team can also get any relevant publications through Interlibrary Loan (ILL) services provided by Chester Fritz Library if they are not in one of the seven libraries.

## 1.5 Environmental and Economic Impacts of the Project while it is Underway

The research team does not anticipate negative impacts on the environment and economy while the project is underway.

## 1.6 Ultimate Technological and Economic Impacts

If this project is successful, it has the potential to be transformative. It will have a huge positive impact on the environment, water, energy, durability of concrete infrastructure, maintenance cost of concrete infrastructure, cost of infrastructure users, etc. Please see the detail in “Value to North Dakota” section.

## 1.7 Why the Project is needed?

Ordinary Portland cement, which is the main binder of ordinary Portland cement-based concrete, represents almost 80% of the total $CO_2$ emissions of concrete *(Shi et al. 2011)*. At an annual production rate of 2.35 billion tons, the cement industry contributes about 5% to global anthropogenic $CO_2$ emissions *(BASF 2008)*. This result in 2.11 million metric tons of $CO_2$ based on the assumption that for each ton of ordinary Portland cement, 0.9 ton of $CO_2$ is released *(Gartner 2004, Meyer 2009)*. Furthermore, ordinary Portland cement clinker production consumes large amounts of energy and involves massive quarrying for raw materials. This is particularly serious in the current context of climate change. Ordinary Portland cement demand is expected to increase almost 200% by 2050 (from 2010 levels), reaching 6000 million tons/year *(Shi et al. 2011)* in the world. There is a critical need to investigate the use of fly ash and nanomaterials-based concrete for sustainable concrete infrastructure

## 2. STANDARDS OF SUCCESS

If fly ash and nanomaterials-based concrete is equivalent to or better than ordinary Portland cement-based concrete in terms of fresh and hardened properties, and durability, then the project will be considered as successful provided that it will be completed within the schedule and budget. An alternative plan will be to determine the maximum amount of ordinary Portland cement that will be replaced by fly ash and nanomaterials in concrete.

## 3. BACKGROUND

### 3.1 Nanotechnology in Ordinary Portland Cement-based Concrete

Because concrete is low cost, moldable, adaptable, fire resistant, and easily engineered, it is the most widely used construction material in the world. Every year more than 10 billion tons of concrete are produced in the world *(Gartner and Macphee 2011)*. Concrete is composed of an amorphous phase, nanometer to micrometer size crystals, and bound water. The properties of concrete exist in, and the degradation mechanisms occur across multiple length scales (Nano to micro to macro), where the properties of each scale derive from those of the next smaller scale (*Jennings et al. 2008, Sanchez et al. 2009, Sanchez and Borwankar 2010*). One can claim that concrete utilizes nanotechnology since it contains Nano-particles as ingredients including Nano-water particles and Nano-air voids as shown in Figure 3 *(Balaguru and Chong 2006)*.

Concrete still requires improvement in its quality and service life. This can be achieved through the use of nanoscience translated by the application of nanotechnology by incorporating nanomaterials in concrete *(Sobolev et al. 2006)*. Some of the benefits of incorporating nanomaterials include: improved strength, durability, self-healing, shrinkage compensation, and elevated resistance to abrasion and fire (*Jo et al. 2007, Hiisken and Brouwers 2008, Fares and Khan 2013*).

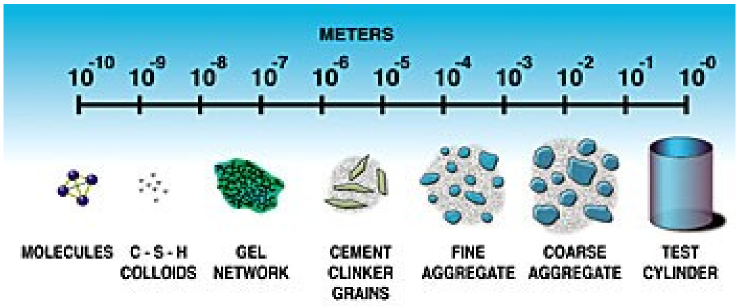

Figure 3. Scales of various constituents of concrete *(Balaguru and Chong 2006)*.

### 3.2 Nanomaterials in Ordinary Portland Cement-based Concrete

Due to the availability of capacity and facility to transfer silica into Nano silica it is the best choice for the practical and extensive nanotechnology applications in concrete *(Zawrah et al. 2009)*. To date concrete-related research has been conducted with Nano silica. The addition of Nano silica increases density; reduces porosity, bleeding and segregation; improves workability, strength, and durability; improves cement paste uniformity and elastic modulus;

and improves the bond between the cement matrix and aggregates *(Sobolev and Ferrada-Gutiérrez 2005, Qing et al. 2007, Gaitero et al. 2008, Lin et al. 2008, Sobolev et al. 2009, Sanchez and Sobolev 2010, Senff et al. 2010, Gaitero et al. 2010)*.

Nano clay materials have shown promise in enhancing mechanical performance, resistance to chloride penetration, and self-compacting properties of concrete, while also reducing permeability *(Birgisson 2006, Kuo et al. 2006, He and Shi 2008, Morsy et al. 2009)*.

### 3.3 Fly Ash and Nanomaterials for Sustainable Concrete Infrastructure

Fly ash has been widely used as supplementary cementitious materials (SCMs) in concrete since it helps to reduce cost, conserve energy and resources, reduce environmental impact, and enhance workability *(Khan 2010)*. Use of SCMs can also improve concrete properties and increase the service life of concrete structures. One drawback of using high volumes of fly ash is a resulting delay in initial setting time due to drastically slow hydration, which reduces the early strength of concrete. However, the ability of nanomaterials to accelerate the rate of hydration of ordinary Portland cement/SCMs blends opens the possibility of significantly lowering the content of cement in concrete *(Corr and Shah 2005, Sato and Beaudoin 2006, Sato and Beaudoin 2007)*, potentially removing this roadblock to reducing greenhouse gas production in the construction industry.

### 3.4 Hydration Reaction

Cement hydration is a complex set of interrelated chemical reactions leading to stiffening of the fresh concrete, followed by strength gain and decreased permeability. Rates are affected by the materials within the system and by the environment to which it is exposed *(Taylor et al. 2007)*.

The hydration process continues in concrete for weeks and years if water is continually present. Cement hydration is a strongly exothermic reaction that takes place in five different stages *(Young 1985)*. The stages are illustrated by a curve that represents changes in heat during the first hours and days of hydration as shown in Figure 4 *(Taylor et al. 2007)*.

Various nanomaterials can improve and densify the cement matrix, leading to improved permeability and strength. The nanomaterials act as "nuclei" of hydration *(Li et al. 2004)*, possess pozzolanic behavior resulting in the consumption of $Ca(OH)_2$ and formation of an "additional" Calcium-Silicate-Hydrate (C-S-H) *(Kang et al. 2001, Collepardi 2002, Kosmatka et al. 2002, Collepardi 2004)*, and can fill the voids in the cement matrix *(Shih et al. 2006)*.

As the hydration rate of fly ash is low, it is necessary to activate it. Nanomaterials improve cementitious properties through two mechanisms: faster pozzolanic reaction due to higher nanomaterials surface area and by acting as centers of nucleation that improve the microstructure. The great reactivity and the pozzolanic nature of nanomaterials further increase the reaction rate by reducing the amount of calcium ions in the hydration water *(Guerrero et al. 2005, Campillo et al. 2007, Chang et al. 2007, Jo et al. 2007, Lindgreen et al 2008, Veras-Agulho et al. 2009, Gaitero et al. 2010, Mondal et al. 2010, Nazari and Riahi 2011, Quercia et al. 2012)*.

## 4. QUALIFICATIONS

### 4.1 Principal Investigator (PI): Daba Gedafa, Ph.D., P.E., M.ASCE

The PI has extensive research, teaching, and industry experience in concrete materials and infrastructure. He has conducted microstructural morphology and elemental composition analysis of concrete using SEM/EDS. He developed performance-related models for concrete pavements in Kansas. He tested mechanical properties of high volume fly ash concrete specimens in the laboratory to validate the models *(Gedafa et al. 2012a)*. The PI also modeled curling of concrete using the finite element method (FEM) *(Gedafa et al. 2012b)*. The PI also investigated the effect of concrete construction environment on the long term performance of jointed plain concrete pavement *(Gedafa et al. 2011)*. The PI also evaluated 15-year performances of special pavement sections (SPS-2), which are concrete pavement sections on Interstate 70 in Kansas *(Khanum et al. 2008)*.

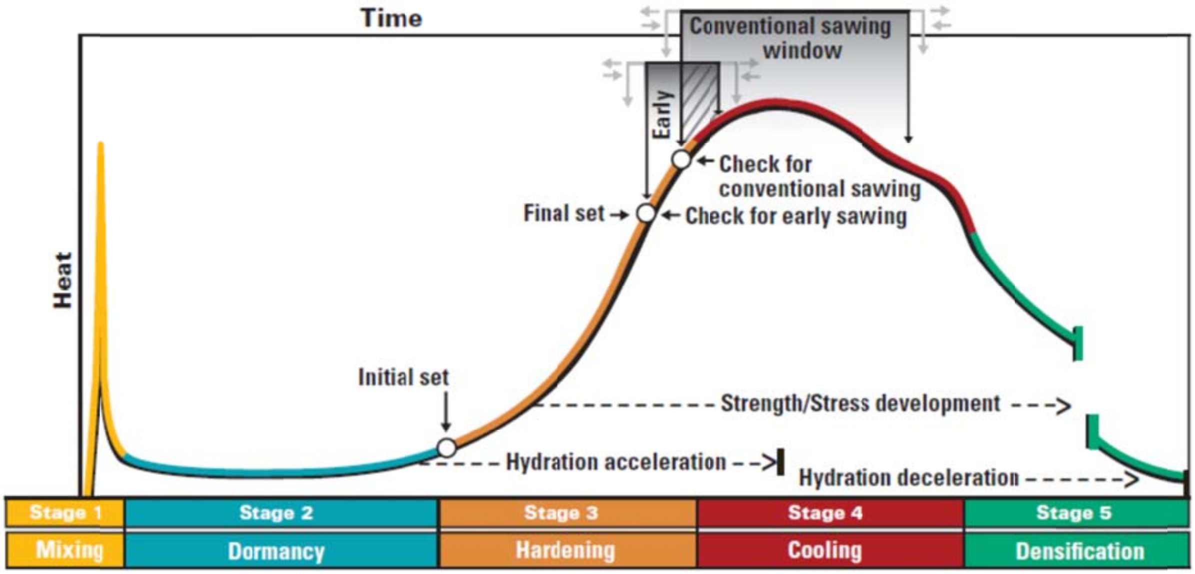

Figure 4. Five stages of hydration *(Taylor et al. 2007)*.

The PI has also taught civil engineering materials course that include material testing in laboratory and report writing at four different institutions. Fresh properties of concrete that have been included in lecture and laboratory are: density, air content, slump, and temperature. Mechanical properties of hardened concrete that have been covered are: compressive strength, flexural strength, tensile strength, and modulus of elasticity. He has been teaching civil engineering materials for the third year at UND, two years at the University of Connecticut, one year at Kansas State University, and one year at Arbaminch University in Ethiopia. He was also the project engineer and acting project manager on the construction of the Durame District

Hospital in Ethiopia. All of these experiences will enable him to investigate the use of fly ash and nanomaterials-based concrete for sustainable concrete infrastructure.

### 4.1.1 Pertinent Publications

1. **Gedafa, D.S.**, Hossain, M., Ingram, L. S., and Kreider, R. (2012). "Performance-related specifications for PCC pavements in Kansas." *ASCE Journal of Materials in Civil Engineering*, 24(4): 479-487.
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## 5. VALUE TO NORTH DAKOTA

The objectives of transportation engineering can be defined as the supply of a safe, durable, economical, and sustainable infrastructure for the movement of goods and people. America's infrastructure received a grade of $D^+$ in 2013, and $3.6 trillion is needed to raise this to B grade by 2020 according to an ASCE report *(ASCE 2013)*. Nanotechnology and modifications at the nanoscale can improve the strength of existing or new materials and provide more cost-effective means of construction *(Halicioglu 2009)*.

One of the most important fields of application for fly ash is Portland cement concrete pavement, where a large quantity of concrete is used and economy is an important factor in concrete pavement construction. Federal Highway Administration (FHWA) has been encouraging the use of fly ash in concrete. When the price of fly ash concrete is equal to, or less than, the price of mixes with only Portland cement, fly ash concretes are given preference if technically appropriate under FHWA guidelines *(Adams 1988)*.

The use of fly ash as a replacement for ordinary Portland cement in concrete can have environmental as well as economic benefits through the reduction of greenhouse gases from the production of ordinary Portland cement, diversion of fly ash from landfills, and reduced use of natural resources used to manufacture ordinary Portland cement *(Jachimovicz and Bentur 2008, Garboczi 2009)*. Durable transportation infrastructure results in a saving of billions of dollars in maintenance cost (savings for federal, state, local, and city highway agencies), reduced vehicle operating cost and travel time (savings for traveling public), and an improved safety for the society (savings for highway agencies and traveling public).

In addition to economic and ecological benefits, the use of fly ash in concrete improves its workability and durability, reduces water demand, corrosion of reinforcing steel, segregation, bleeding, heat evolution and permeability, inhibits alkali-aggregate reaction, and enhances sulfate resistance *(Helmuth 1987)*. The benefits of using fly ash instead of Portland cement in concrete are described in greater detail.

### 5.1 Landfill

By using fly ash instead of disposing of it in landfills, the environmental degradation and energy costs associated with mining virgin materials can be avoided. Environmentally and economically it makes more sense to use existing materials than to mine new ones.

- A savings of $320,000 in landfill disposal costs for every 85,000 tons of fly ash used in making concrete products *(Great River Energy 2003).*

- America is able to reduce the need for additional landfills by recycling fly ash. For each ton recycled, space equivalent to 455 days' worth of solid waste is saved in a landfill *(EPA 2008)*.

### 5.2 Energy and Environment

Stronger, longer-lasting structures that save taxpayer dollars and minimize environmental impacts can be built using fly ash. For every ton of fly ash used in place of Portland cement about a ton of carbon dioxide is prevented from entering the Earth's atmosphere. Also, it takes the equivalent of 55 gallons of oil to produce a single ton of cement. The energy saved by using fly ash is equal to 24 days electricity consumption of an average home. Beneficial use of fly ash in concrete production reduced U.S. greenhouse gas emissions by as much as 15 million tons (Mt) in 2007 alone. Using fly ash also saves the energy needed to extract and process other materials for these same uses *(EPA 2008)*.

### 5.3 Water

Concrete made with fly ash requires at least 10 percent less water to produce a long lasting product, conserving a limited resource, while also reducing a project's water and equipment costs. This is beneficial for the State of North Dakota and its people, especially in the western part of the state where water demand for the oil wells is high.

### 5.4 Economic Impact

Federal concrete projects used an estimated 5.3 Mt of fly ash in 2004 and 2005 combined. This substitution yields a number of environmental benefits, including avoided energy use of approximately 25 billion megajoules; avoided water consumption of two billion liters; and avoided carbon dioxide equivalent emissions of 3.8 Mt. Energy and water savings represent two significant impacts that can be monetized using market prices. Results indicate that the beneficial use of coal fly ash in 2004 and 2005 resulted in energy savings valued at approximately $700 million, and water savings valued at approximately $1.2 million *(EPA 2008)*. Table 3 shows the summary of savings per ton of fly ash in concrete.

Table 3. Energy Savings and Life Cycle Impacts of One Ton of Fly Ash in Concrete *(EPA 2008)*

| **Metric Measurement** | **Amount** |
|---|---|
| Energy Savings in dollars | $129.10 |
| Water savings | 99.4 gallons |
| Avoided total $CO_2$ equivalent greenhouse gases | apx. 0.80 tons (ave.) per ton of portland cement |
| Avoided gasoline consumption | 82 gallons |
| Avoided oil consumption | 53.5 gallons |

The Portland Cement Association (PCA) reports that in 2005, before the onset of the current fiscal problems, the US consumed approximately 122 Mt of cement *(PCA 2013)*. The extent of the damage inflicted by the current economic downturn on the US cement industry can be seen by looking at cement consumption statistics from 2005, the peak of US cement demand, and 2010. Many other states saw decreases well into double-digits over the same period, with only two states seeing a net increase in cement consumption over the same time period. These were Louisiana, where consumption increased by over a quarter, and North Dakota, where consumption was up by 17%. Neither of these states has its own integrated cement plant. North Dakota's cement consumption was 0.8 Mt in 2012, a 46% increase from 2011. Cement consumption is expected to increase at a faster rate due to the economic growth in North Dakota. Portland Cement Association (PCA) estimates US cement consumption will be 107 Mt by 2016.

In 2007, the United States produced 131 Mt of coal combustion products. While 43 percent were used beneficially, nearly 75 Mt were disposed of *(Coal Ash Facts 2013)*. Since 2003, Great River Energy has been a Champion of EPA's Coal Combustion Products Partnership (C2P2) to promote the benefits of coal combustion products – including fly ash. As a C2P2 Champion, Great River Energy has developed and committed to goals to increase the use of fly ash. Great River Energy produces about 440,000 tons of marketable fly ash per year at its Coal Creek Station. Fly ash sales have steadily increased *(Great River Energy 2003)*.

The cost of a ton of fly ash is often half the price of Portland cement. Using fly ash instead of Portland cement can reduce the cost of a concrete in a project while improving its overall performance and durability. The price of fly ash and ordinary Portland cement per ton is $85 and $165, respectively according to Lafarge in Grand Forks. Table 4 shows the net increase in benefits in millions of dollars in fly ash sale assuming 1Mt and 110Mt cement consumption in North Dakota and US, respectively. For example, if 50% of Portland cement is replaced by fly ash and there is a 20% increase in the price of fly ash, the benefit will increase by 10.2 and 1122 million dollars in North Dakota and US, respectively. This is without considering other environmental, energy, water, decrease in maintenance cost, etc. This is a direct benefit for coal plant owners and Lignite Research Council.

## 6. MANAGEMENT

One graduate research assistant will work on this project under the supervision of the PI. The research team will submit quarterly progress reports and make sure that the project will be complete within the schedule and budget.

Table 4. Increase in Benefit for Certain Increase in Fly Ash Price as it Replaces Cement

| **% Replacement** | **% Increase in Fly Ash Price in North Dakota** | | | | | **% Increase in Fly Ash Price in US** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **10** | **20** | **30** | **40** | **50** | **10** | **20** | **30** | **40** | **50** |
| 10 | 0.85 | 1.7 | 2.55 | 2.55 | 4.25 | 93.5 | 187 | 280.5 | 280.5 | 467.5 |
| 20 | 1.7 | 3.4 | 5.1 | 6.8 | 8.5 | 187 | 374 | 561 | 748 | 935 |
| 30 | 2.55 | 5.1 | 7.65 | 10.2 | 12.75 | 280.5 | 561 | 841.5 | 1122 | 1402.5 |
| 40 | 5.1 | 7.65 | 10.2 | 12.75 | 17 | 561 | 841.5 | 1122 | 1402.5 | 1870 |
| 50 | 7.65 | 10.2 | 12.75 | 17 | 21.25 | 841.5 | 1122 | 1402.5 | 1870 | 2337.5 |
| 60 | 10.2 | 12.75 | 17 | 21.25 | 25.5 | 1122 | 1402.5 | 1870 | 2337.5 | 2805 |
| 70 | 12.75 | 17 | 21.25 | 25.5 | 29.75 | 1402.5 | 1870 | 2337.5 | 2805 | 3272.5 |
| 80 | 17 | 21.25 | 25.5 | 29.75 | 34 | 1870 | 2337.5 | 2805 | 3272.5 | 3740 |
| 90 | 21.25 | 25.5 | 29.75 | 34 | 38.25 | 2337.5 | 2805 | 3272.5 | 3740 | 4207.5 |
| 100 | 25.5 | 29.75 | 34 | 38.25 | 42.5 | 2805 | 3272.5 | 3740 | 4207.5 | 4675 |

## 7. TIMETABLE

Tentative project start and completion date will be February 1, 2014 and January 31, 2015, respectively. The research team shall submit to the commission quarterly reports summarizing the project's accomplishments and expenditures to date. The research team will submit quarterly reports on April 30, 2014; July 31, 2014; and October 31, 2014 assuming that the project will start on February 1, 2014. The research team will follow the timing of the reports that will be specified in the contract if this project is funded.

The research team will submit comprehensive final report to the commission within the time specified in the contract. The report will include a single page project summary describing the purpose of the project, the work accomplished, the project's results, and the potential applications of the project. The rest of the report will explain these subjects in detail as well as the total costs of the project, a summary fiscal accounting of the entire project, any plans for developing or putting to commercial use the results of the project, and whether and in what manner the project met or failed to meet the standards referred to in subsection 7 of section 43-03-04-01.

## 8. BUDGET

Table 5 shows an itemized project cost that include the money requested from North Dakota Industrial Commission (NDIC) and matching fund. Principal investigator, Dr. Gedafa and one quarter-time graduate research assistant will work on this project. The research team would like to request about 24% of the total project cost from NDIC, which is the minimum amount of money necessary to achieve the project's objectives. If less funding is available than that requested, all the objectives may not be met and the results may be inconclusive.

### 8.1 Budget Justification

#### 8.1.2 Salary

About half of the salary for the PI and graduate research assistant has been requested from North Dakota Industrial Commission (NDIC) for their effort in this project.

#### 8.1.3 Fringe Benefits

PI's fringe benefit has been calculated as 20% of the salary requested.

#### 8.1.4 Materials and Supplies

Budget has been requested for materials: nanomaterials, fly ash, aggregates, cement, etc. The supplies include molds to make specimens for strength tests, plate pads for compressive strength test, oil for universal testing machine, etc.

**Table 5 Budget for the Project**

|  | NDIC | Matching Fund |  | Total |
|---|---|---|---|---|
|  |  | UND Civil Engineering | Great River Energy |  |
| **Salary** |  |  |  |  |
| Dr. Gedafa (PI) | 4000 |  | 4243 | 8243 |
| Grad. Res. Ass't | 5000 |  | 5200 | 10200 |
| **Total Salary** | **9000** | **0** | **9443** | **18443** |
|  |  |  |  |  |
| **Fringe Benefits** |  |  |  |  |
| Dr. Gedafa (PI) | 800 | 0 | 849 | 1649 |
| Grad. Res. Ass't |  | 796 |  | 796 |
| **Total Fringe Benefits** | **800** | **796** | **849** | **2445** |
|  |  |  |  |  |
| Grad. Student Tuition |  | 4,984 |  | 4984 |
|  |  |  |  |  |
| Equipment |  | 25000 |  | 25000 |
|  |  |  |  |  |
| Materials and Supplies | 500 |  | 328 | 828 |
|  |  |  |  |  |
| Travel | 250 |  | 250 | 500 |
|  |  |  |  |  |
| **Total Direct Cost (TDC)** | **10550** | **30780** | **10870** | **52200** |
|  |  |  |  |  |
| **Modified Total Direct Costs (MTDC)** | **10550** | **796** | **10870** | **22216** |
|  |  |  |  |  |
| **Indirect Cost (38% of MTDC)** | **4009** | **302** | **4130** | **8442** |
|  |  |  |  |  |
| **Total Project Cost** | **14559** | **31082** | **15000** | **60642** |

### 8.1.5 Travel

Travel to Lignite Research Council's meeting to make presentation if necessary. It may be used to travel to national and/or international conference (s) to make presentations based on research results.

#### 8.1.6 Indirect Cost

Indirect cost has been calculated as 38% of the modified total direct cost (MTDC), which excludes equipment cost and graduate student tuition.

## 9. MATCHING FUNDS

Matching funds will be provided by Civil Engineering Department at the University of North Dakota (about 51% of the total project cost) and Great River Energy (about 25% of the total project cost).

### 9.1 Budget Justification

#### 9.1.1 Salary

About half of the salary for the PI and graduate research assistant will be covered by Great River Energy if the project is funded by North Dakota Industrial Commission.

#### 9.1.2 Fringe Benefits

PI's fringe benefit has been calculated as 20% of the salary requested. The fringe benefit for the graduate research assistant will be covered by UND civil engineering department.

#### 9.1.3 Graduate Student Tuition

UND civil engineering department will cover graduate student tuition (15 credit hours) for the project period.

### 9.1.4 Equipment

UND civil engineering will purchase a new freeze-thaw cabinet for this project to determine the durability of fly ash and nanomaterials-based concrete.

### 9.1.5 Materials and Supplies

Part of materials and supplies cost will be covered by Great River Energy.

### 9.1.6 Travel

Half of the travel cost to Lignite Research Council's meeting to make presentation if necessary will be covered by Great River Energy. It may be used to travel to national and/or international conference (s) to make presentations based on research results.

### 9.1.7 Indirect Cost

Indirect cost has been calculated as 38% of the modified total direct cost (MTDC), which excludes equipment cost and tuition.

## 10. TAX LIABILITY

No outstanding tax liability owed to the state of North Dakota or any of its political subdivisions.

## 11. CONFIDENTIAL INFORMATION

There is no confidential information in this proposal.

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September 27, 2013

Daba S. Gedafa, Ph.D., P.E., M.ASCE
Assistant Professor
Civil Engineering Department
University of North Dakota
Upson II Room 260K
243 Centennial Drive Stop 8115
Grand Forks, ND 58202-8115

Dear Professor Gedafa:

Great River Energy is supportive of your research to investigate whether or not we can fully replace Portland cement with fly ash and nanomaterials in concrete. An alternative plan is to determine the maximum amount of Portland cement that can be replaced with fly ash and nanomaterials. Great River Energy will commit $15,000 to support the project if you are successful obtaining the balance of the funding to proceed.

Sincerely,

GREAT RIVER ENERGY

John Weeda

John Weeda
Director of ND Generation