

Enzyme-Induced Carbonate Precipitation for the Mitigation of Fugitive Dust

by

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A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved April 2014 by the
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May 2014

ABSTRACT

Enzyme-Induced Carbonate Precipitation (EICP) using a plant-derived form of the urease enzyme to induce the precipitation of calcium carbonate (CaCO_3) shows promise as a method of stabilizing soil for the mitigation of fugitive dust. Fugitive dust is a significant problem in Arizona, particularly in Maricopa County. Maricopa County is an EPA air quality non-attainment zone, due primarily to fugitive dust, which presents a significant health risk to local residents. Conventional methods for fugitive dust control, including the application of water, are either ineffective in arid climates, very expensive, or limited to short term stabilization. Due to these limitations, engineers are searching for new and more effective ways to stabilize the soil and reduce wind erosion. EICP employs urea hydrolysis, a process in which carbonate precipitation is catalyzed by the urease enzyme, a widely occurring protein found in many plants and microorganisms. Wind tunnel experiments were conducted in the ASU/NASA Planetary Wind Tunnel to evaluate the use of EICP as a means to stabilize soil against fugitive dust emission. Three different soils were tested, including a native Arizona silty-sand, a uniform fine to medium grained silica sand, and mine tailings from a mine in southern Arizona. The test soil was loosely placed in specimen container and the surface was sprayed with an aqueous solution containing urea, calcium chloride, and urease enzyme. After a short period of time to allow for CaCO_3 precipitation, the specimens were tested in the wind tunnel. The completed tests show that EICP can increase the detachment velocity compared to bare or wetted soil and thus holds promise as a means of mitigating fugitive dust emissions.

DEDICATION

This thesis is dedicated to my parents, Mark and Carol Knorr, who have provided both emotional and financial support in my academic career. Without their guidance and life lessons I would not have been able to reach my goals.

ACKNOWLEDGMENTS

I would like to express my gratitude to my advisor, Dr. Edward Kavazanjian Jr. for giving me the opportunity to be his pupil. His guidance and the knowledge he has passed onto me have been imperative in me reaching my educational goals. You have been a true leader to me in my education, and I look up to you with the utmost respect.

I would also like to thank Nasser Hamdan for all his help and hard work. He taught me everything about EICP, and without him this research would not have been possible.

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CHAPTER 1

Introduction and Background

1.1 Objective

The purpose of this study is to determine the effectiveness of enzyme-induced carbonate precipitation (EICP) as a means of fugitive dust mitigation. Fugitive dust is a significant problem throughout the southwestern US and other arid and semi-arid regions around the world, and particularly in Maricopa County, Arizona. Maricopa County is an EPA air quality non-attainment zone due primarily to fugitive dust, which presents a significant health risk to local residents. Penalties for failure to comply with EPA air quality standards can include significant fines and the loss of all federal transportation funds. EICP employs urea hydrolysis, a process in which calcium carbonate (CaCO_3) precipitation from a solution of calcium chloride (CaCl_2) and urea is catalyzed by the urease enzyme, a widely occurring protein found in many plants and microorganisms. Wind tunnel experiments are being conducted to determine if EICP can effectively cement soil particles together to reduce their tendency to detach as fugitive dust.

1.2 Background

The 21st century has brought many challenges to all facets of society including engineering practice. The focus has shifted to the use of sustainable or “green” materials and processes. This is being done to help protect the environment and to reduce the consumption of earth’s natural resources. When it comes to the field of geotechnical engineering, the most common “green” practices are applied to soil improvement. Popular methods of soil improvement usually involve heavy machinery and heavy energy consumption. When engineers started to view the soil as a “living ecosystem” they realized the possibilities of sustainable solutions to soil improvement problems (DeJong, et. al. 2011). Realizing these possibilities requires employing the help of chemists and biologists to develop new bio-geotechnical techniques for soil improvement (DeJong et. al, 2011). One popular technique that has been developed is using urea hydrolysis to induce calcium carbonate precipitation in soil. Urea hydrolysis involves using calcium chloride, urea, and some form of urease enzyme to induce carbonate precipitation within

the soil matrix and cement the soil grains together. This soil cementation has many benefits, including an increase in shear strength and increased liquefaction resistance.

This thesis focuses on the research of using urea hydrolysis to help control erosion. Most previous work on urea hydrolysis as a soil improvement process employs microbial urease and is commonly referred as microbially induced carbonate precipitation (MICP). The work in this dissertation employs enzyme induced carbonate (or calcite) precipitation (EICP). EICP uses a plant-derived form of the urease enzyme to induce the precipitation of calcium carbonate (CaCO_3).

This thesis investigates the use of EICP as a method of stabilizing soil for the mitigation of fugitive dust. Fugitive dust is a significant problem in Arizona, particularly in Maricopa County. Maricopa County is an EPA air quality non-attainment zone, due primarily to fugitive dust, which presents a significant health risk to local residents. Penalties for failure to comply with EPA air quality standards can include significant fines and the loss of all federal transportation funds. Conventional methods for fugitive dust control, including the application of water, are either ineffective in arid climates, very expensive, or limited to short term stabilization. Furthermore, these methods tend not to be very sustainable, as they consume a lot of energy and/or potable water. Due to these limitations, engineers are searching for new and more effective ways to stabilize the soil and reduce wind erosion.

1.3 Scope of Work

The scope of this thesis is to try and determine the effectiveness of EICP as a means of surficial soil stabilization. Wind tunnel experiments were conducted in the Arizona State University (ASU)/National Aeronautics and Space Administration (NASA) Planetary Wind Tunnel to evaluate the use of EICP as a means to stabilize soil against fugitive dust emission. This wind tunnel was designed specifically to measure the detachment velocity of soil particles subject to wind loading. Three different soils were tested, including a native Arizona silty-sand, a uniform fine to medium grained silica sand, and mine tailings from a mine in southern Arizona. The test soil was loosely placed in a specimen container level with the top of the container and the surface was sprayed with an aqueous solution containing urea, calcium chloride, and urease enzyme. After a

short period of time to allow for calcium carbonate (CaCO_3) precipitation, the specimens were placed in the wind tunnel. The wind speed was increased incrementally until there was visual detachment (lift off) of soil particles.

The ultimate goal of this research is to determine if EICP is a sustainable fugitive dust mitigation technique that can be applied in the real world. Applications of this technique include construction sites, mine sites, and anywhere there is surficial soil that needs to be stabilized. In order to achieve this goal, the process must be developed into a simple and cost effective process. The “gold standard” of erosion control is soil that is thoroughly wetted. To achieve this gold standard in a cost effective manner, a variety of precipitated carbonate concentrations must be tested to determine the lowest concentration that can induce cementation with equal effectiveness to wetting the soil. The lower the concentration, the lower the cost. In addition to the determination of the minimum required concentration, this research involved experimenting with different methods of application of the cementation method to the soil. Application techniques investigated herein involved applying the cementing solution and the enzyme solution either together or separately and applying the solution through a variety of devices. Supplemental testing was done on EICP-treated samples to evaluate the crust strength over time the resistance to water erosion, the durability of the samples, and the shear strength of the stabilized soil crust formed by EICP.

Tests were performed on three different soils. The first soil was native Arizona silty sand that was “manufactured” via sieve analysis to separate the large gravel-sized particles and the finer particles. The second soil was a uniform medium to fine grained silica sand. The third soil was mine tailings from a mine in southern Arizona.

1.4 Organization

This thesis was organized into the following six chapters, including this introductory chapter that discusses the purpose of this study along with a brief background and overview of the research conducted. Chapter 2 presents a literature review to provide background information that is relevant to the subsequent chapters of the dissertation. Chapter 3 is the experimentation plan that was developed for this research, including soil types and soil property testing. Chapter 4 presents the wind

tunnel testing program. Chapter 5 presents the supplemental testing that was done (in addition to wind tunnel testing) to characterize the EICP-stabilized soil. Chapter 6 presents a summary of the work and conclusions drawn from this study along with recommendations for future study of the use of EICP for mitigation of fugitive dust.

CHAPTER 2

Literature Review

2.1 Introduction

EICP is a soil improvement technique that falls within the field of biogeotechnical engineering. Biogeotechnical engineering is a relatively new sub-discipline within geotechnical engineering. Biogeotechnical engineering techniques have steadily gained attention from geotechnical engineers within the last few years. Interest in biogeotechnical techniques started when engineers began to see that soil mechanics alone was insufficient to address many practical problems (DeJong, et al. 2013). Modern construction techniques developed to address practical problems may often cause adverse environmental impacts.

As geotechnical engineers looked for more environmentally friendly or “green” options for soil improvement, they started to realize that the soil is a “living ecosystem” in which potentially beneficial biological and chemical processes are occurring all the time. In the 1970’s, work done by Mitchell (Mitchell, 1975) recognized the important role that chemistry plays in fine-grained soil behavior (DeJong, J.T. et al. 2013). The idea of biogeotechnical engineering started spreading through the field of geotechnical engineering, and in 2005, biogeotechnical engineering was identified as an important research topic by the National Research Council (DeJong, et al. 2013). Mitchell and Santamarina (Mitchell and Santamarina 2005) then presented the first detailed discussion of biogeotechnical engineering (DeJong, et al. 2013). Since that time, there have been several international biogeotechnical engineering workshops (e.g. in 2008 and 2011) and over 100 technical papers have been written on the topic (DeJong, et al. 2013). These activities have included contribution to many areas of biogeotechnical engineering. Perhaps the major topic of interest in these biogeotechnical studies has been the improvement of soil via carbonate precipitation induced by urea hydrolysis, with most studies focusing on MICP.

2.2 Issues with Fugitive Dust

Wind erosion causes soil particles to be lifted from their natural place, causing

fugitive dust problems. It is estimated that wind induced soil transports more than 500×10^6 metric tons of fugitive dust annually (Alsanad, 2011). Fugitive dust can impact the environment and cause adverse health side effects. Fugitive dust has caused vehicle accidents due to reduced visibility, caused damage to homes, destroyed landscaping, and most importantly, increased the incidence of respiratory and cardiovascular conditions in the general population (USDA, 2013). Fugitive dust is a significant problem, specifically in Arizona. Over the past few years, construction sites around Maricopa County have been failing their air quality inspections. This accumulation of air quality inspection failures has caused the Environmental Protection Agency (EPA) to take action against the state of Arizona. The EPA fined the state of Arizona millions of dollars due to their lack of effective fugitive dust control. In turn, the state of Arizona is charging construction companies to pay for the state fines acquired from the EPA. In addition to the fines however, Arizona is being threatened with a loss of federal highway funds. This is a substantial issue for Arizona, and that is why they are allocating funds to implement new and effective methods of fugitive dust control.

Current practice of fugitive dust control consists of constantly spraying the site with water, or using extremely expensive polymers to reduce erosion. These options work, but they are not cost effective. EICP is an effective, relatively cost effective, and environmentally friendly option for fugitive dust control. With further research it could become the new gold standard for erosion control. Water is considered the current “gold standard” of dust control, but in an arid environment it requires multiple passes over the course of a day to suppress dust. EICP stabilizes fugitive dust in a dry state. This means that our goal is to achieve a detachment velocity similar to that of water when we apply EICP solution to the soil. Detachment velocity is simply the velocity of wind moving over a surface that will cause soil particles to detach from their original surface. Typically the soils that have low detachment velocities are most susceptible to fugitive dust propagation are fine-grained soils. However, some very fine clays will have some cohesion that will resist detachment more than a silty soil. The soil in Arizona tends to be very silty, and that is why fugitive dust is such an issue in this area.

2.3 Urea Hydrolysis for EICP

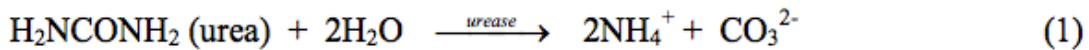
The purpose of urea hydrolysis is to induce carbonate precipitation in the soil. There are multiple ways to induce carbonate precipitation in soils. Some methods include urea hydrolysis, denitrification, sulphate reduction, inducing dolomite precipitation, iron reduction, and inducing ankerite precipitation (DeJong, et al. 2013). However, urea hydrolysis is the most energy efficient of all these processes (DeJong, et al. 2013). The process of urease hydrolysis uses calcium chloride, urea, and urease enzyme to induce carbonate precipitation in the soil. The precipitated carbonate fills void spaces within the soil, and cements the soil together. When the calcium chloride and urea are mixed together, they are a stable compound and no reaction takes place. The key ingredient that drives the process of bio-cementation is the urease enzyme.

Urease can come from a variety of sources. The two most popular sources are microorganisms and plants. Studies using both microbe and plant based urease have been completed and have shown that they can induce carbonate precipitation. Urea hydrolysis did not get its start as a method to control fugitive dust. Carbonate precipitation from urea hydrolysis was proposed as an engineering technique in the early 1990s. It was called “Carbonate in Place” or CIP, and it was a method used in the oil industry for recovering oil. The carbonate that was produced via urea hydrolysis was used to clog up the pore space of soils around an oil-drilling unit. The clogging of pores around the drill caused oil to flow out of the hole being drilled, and not moving laterally in the soil (Ferris and Setehmeir 1992; Gollapudi et al. 1995; Nemati and Voordouw 2005).

After the development of CIP, carbonate precipitation from urea hydrolysis was used in a variety of other applications, including restoration of calcareous stone materials (Tiano et al. 1995; Castanier et al. 2000; Stocks-Fisher et al. 1999; Rodriguez- Navarro et al. 2003), bioremediation (Ferris 2003; Fujita et al. et al. 2001), wastewater treatment (Hammes et al. 2003), and strengthening of concrete (Ramachandran et al. 2001). More recently, the focus on engineering application of carbonate precipitation from urea hydrolysis has shifted towards the field of geotechnical engineering.

2.4 The Chemistry of Urea Hydrolysis

As stated previously, EICP is induced by urease enzyme reacting in solution with calcium chloride and urea. Calcium chloride (CaCl_2) is a salt and is the calcium source for the precipitated calcium carbonate. Urea (H_2NCONH_2) is a hydrogen source that provides the energy necessary for urease hydrolysis. The precipitation of calcium carbonate by hydrolysis of urea is a two-part reaction. In the first reaction (1) urease catalyzes a reaction with the urea and water that produces ammonium and carbonate ions:



This first reaction raises the pH of the solution. This raise in pH creates an optimum condition for carbonate precipitation. The NH_4 and CO_3 products from this reaction actually represent the final product of a series of reactions. The NH_4 (Ammonium, an acid) actually starts out as NH_3 (Ammonia). When the ammonia reacts with water, it creates OH^- ions, which raise the pH of the system. This raise in pH causes the carbonate speciation. The carbonate speciation plot below shows how CO_3 in water is dependent upon pH. When the pH is high, we are more likely to produce carbonate “ CO_3^{2-} ”.

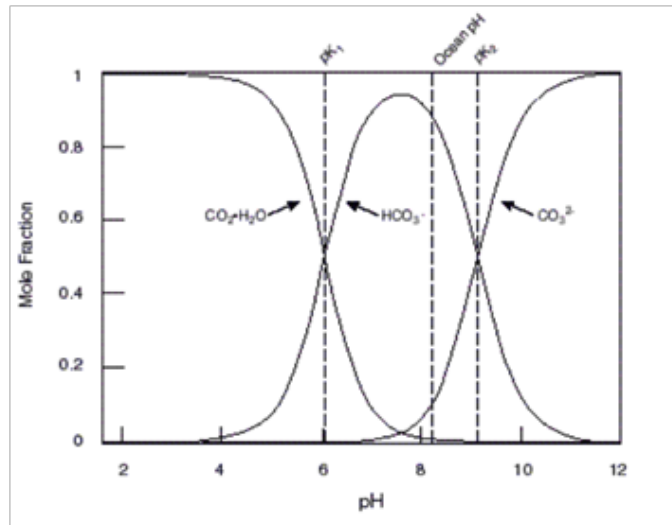


Figure 1: Speciation of Total Carbonate CO_3 in seawater vs. pH (Jacob, 1999).

Once this reaction is finished, reaction (2) begins.



This reaction combines the calcium ions (Ca^{2+}) from the calcium chloride and the carbonate ions (CO_3^{2-}) from equation (1) to create calcium carbonate, which precipitates from solution when the pH and carbonate content are high enough, (Meyer et al. 2011).

2.5 Microbially Induced Carbonate Precipitation (MICP) Research

2.5.1 Introduction

Carbonate precipitation via urea hydrolysis can be carried out by two different processes. The processes differ with respect to the source of the urease enzyme. One process uses microorganisms and the other uses plants as the urease source. Most of the recent geotechnical research uses microbes as the source of urease. *Sporosarcina pasteurii* (formally *Bacillus pasteurii*) is an alkalophilic bacterium that secretes a highly active urease enzyme (DeJong, et al. 2013). These bacterium are very common, but they must be grown, harvested, and mixed into solution in order to harness the urease. Using microbes, including *Sporosarcina pasteurii*, as a urease source is commonly referred to as microbially induced carbonate precipitation or MICP.

2.5.2 MICP Studies on Soil Strength and Liquefaction Resistance

Before MICP was researched for use in soil erosion control, it was studied to see how it affects soil behavior. There have been multiple studies to determine the shear strength and liquefaction resistance of soil due to MICP.

MICP Research by Whiffin and the Delft Group

One early research project on MICP for geotechnical purposes was conducted by Victoria Whiffin in the Netherlands (Whiffin et al. 2007). To evaluate MICP as a soil strengthening process, a five meter sand column was treated with *Sporosarcina pasteurii* bacteria under conditions that were realistic for field applications. The five-meter column was positioned vertically and packed with 125–250 μm Itterbeck sand. The column was

positioned vertically with downward flow direction to avoid any settling of the packing material and generation of preferential flow paths that may occur if the column was positioned horizontally. Each end of the column was packed with a Scotch Brite scouring pad in addition to 8cm of filler gravel up against the sand. Packing of the sand column was conducted under water to the required density to avoid the inclusion of air pockets. There were also five water pressure transducers fitted to the pipe in order to monitor water pressure inside the column at 0, 0.5, 1, 2 and 3 m from the top of the column.

The sand column that Whiffin et al. (2007) prepared had ports on the side to inject in bacteria. There were 10 pore fluid sampling ports spaced at .25 m and .5 m, then spaced at intervals of .5 meters over the length of the entire PVC tube. Fluid reservoirs containing the injected fluids of water, bacteria, calcium chloride and urea were connected at the top of the column. A pump was installed at the bottom of the column to regulate the outflow rate and hydraulic head between free gravity flow of 1 L/h at a hydraulic head of 5 m when the pump was fully open and zero when the pump was fully closed. During the experiments the flow rate was kept constant at approximately 0.35 L/h.

In order to immobilize bacteria in the column for use in subsequent cementation, Whiffin et al. (2007) conducted a 2-phase injection. First bacteria were injected to fill the column volume at multiple injection ports. After the bacteria were injected, a 1.1 molar solution of urea and calcium chloride was injected into the same ports. Under the constant flow conditions during injection, the movement of the front of reaction fluid (1.1 M urea/calcium) could be followed in the column. The first appearance of ammonium in the sampling ports along the column length were measured and matched with the residence time that the fluid had been present in the column. This showed evidence that not all of the calcium chloride and urea solution were making their way all the way to the bottom of the column. This caused more cementation near the injection ports.

After MICP was allowed to take place, Whiffin et al. (2007) cut the column into 25 cm sections. Compressive strength and stiffness of the sections were determined by single-stage confined drained triaxial tests with a confining pressure of 50 kPa. Porosity was determined from the wet and dry densities of the samples after strength testing. Permeability was measured by a constant head test. After testing the samples to failure,

they were retested to determine the strength of the sand after the bonds were broken. The results of the strength tests are shown in Figure 2. From this figure we can see that carbonate content has a large affect on the confined compressive strength of the soil. Low calcium carbonate concentrations (below 60 kg/m³) did not significantly improve the strength of the samples. Higher calcium carbonate contents showed a significant improvement in strength relative to untreated sand (Whiffin et al. 2007).

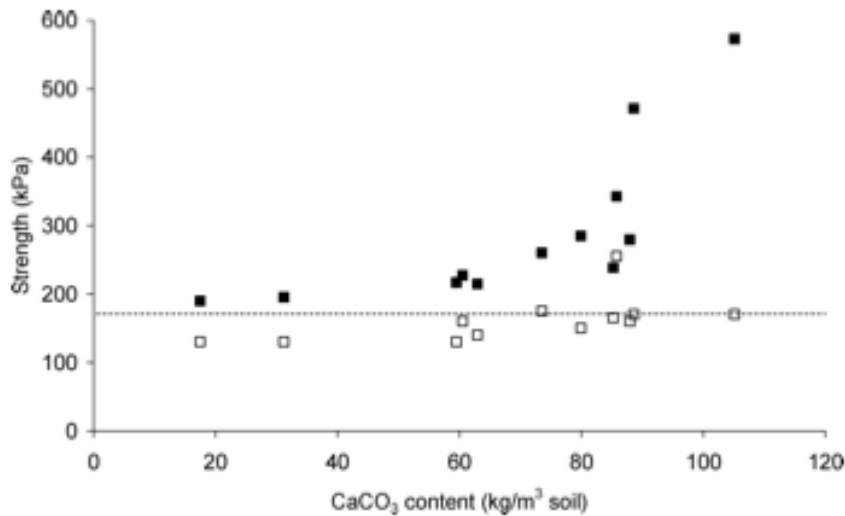


Figure 2: Combined compressive strength (black) and residual compressive strength after failure (white) versus calcium carbonate content. Confining pressure was 50 kPa (Whiffin et al. 2007).

MICP Research at the University of California-Davis.

Soil liquefaction is a significant issue that is encountered in geotechnical engineering practice. In 2012, researchers at the University of California, Davis did centrifuge testing on soils cemented using MICP (Montoya, et al. 2012). Using the Schaevitz 1-m radius centrifuge at the Center for Geotechnical Modeling at UC Davis, researchers were able to mimic earthquake-like conditions on samples of Ottawa 50-70 sand. The centrifuge model was instrumented to measure accelerations, pore pressures, and shear wave velocity. Tests were performed at a centrifugal acceleration of 50 g, and the shaking method for each centrifuge test consisted of sine waves at a prototype frequency of 2 Hz. They would then increase the horizontal accelerations from about .1 to

.7 g at the base of the centrifuge container. The method for cementation used *Sporosarcina pasteurii* just like Whiffin et al. (2007) used in their tests. The MICP was done by allowing a mixture of bacteria and urea to free-drain through the soil and out six ports at the container base for one treatment. Then after the first injection, a 0.5 M solution of calcium chloride was introduced repeatedly every 4-6 hours until the sample reached a target shear wave velocity. The target shear wave velocity for the cemented sample was 650 m/s while the shear wave velocity for the untreated sand was 150 m/s. The researchers saw that compared to the untreated sand, the cemented sample had a large decrease in excess generated pore pressures due to seismic loading, an increase in soil stiffness, and a decrease in vertical strains (Montoya, et al. 2012). A comparison of the vertical strains in these tests is shown in Figure 3.

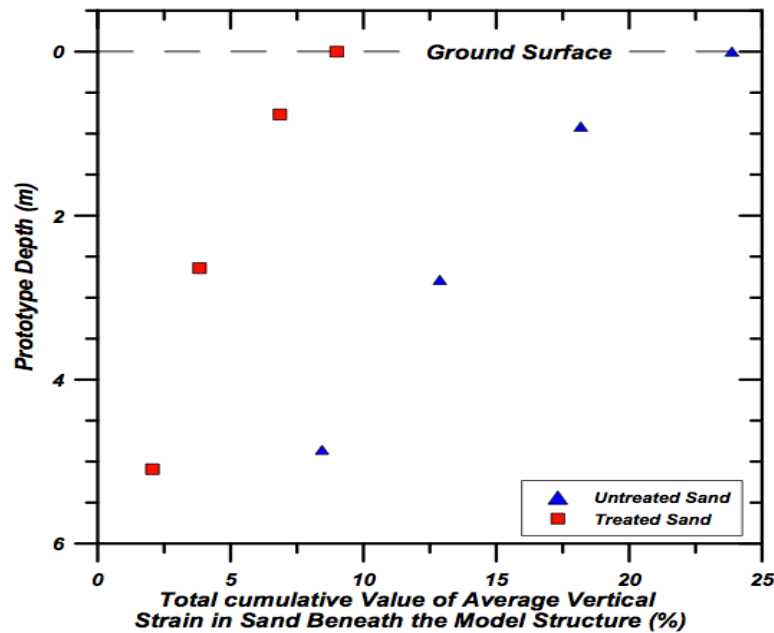


Figure 3: Average vertical strains (%) throughout the sample depth (Montoya, B.M. et al. 2012)

Particle rearrangement due to seismic loading, the primary cause of liquefaction in saturated sand, in the cemented soil sample was reduced compared to the untreated sample due to the calcium carbonate precipitation. This decreased excess pore water pressures within the treated sample and increased the soil's liquefaction resistance compared to the untreated soil (Montoya, B.M. et al. 2012).

2.5.3 MICP Erosion Control Research

Researchers at South Dakota School of Mines and Technology (SDSMT) investigated the use of MICP for erosion control. This research was geared specifically towards determining the erosion control benefits that can be reaped from using MICP. The SDSMT research looked at the effects of bacterial concentration, temperature, humidity, and preparation methods on the level of wind erosion that occurs in well-graded sand (Meyer et al. 2011). Soil pans were filled with samples of a well-graded sand (Unified Soil Classification: SW). Half of the soil samples were left in their original state and the other half were washed in order to see the effects of removing the finer soil particles. Meyer used *Sporosarcina pasteurii* as his source of urease for these tests. Five (5) different bacteria concentrations, from 1×10^5 cells/mL to 1×10^9 cells/mL, were used in 5 series of tests. Meyer et al. increased the concentration by one order of magnitude for each series of tests. In addition to the change in bacterial concentrations, the volume of the urea/calcium chloride solution was also varied from 1-5 mL. Testing was done at temperatures of 20, 30, and 45 degrees Celsius. Tests were also conducted at 20% relative humidity and 100% relative humidity.

After the soil specimens are prepared they were placed into a large-scale wind tunnel to determine mass loss and aerosol production rate under wind loading (Meyer et al. 2011). The large-scale wind tunnel had a height of 0.51 m, a width of 0.51 m, and a length of 8.5 m (Meyer et al. 2011). Wind speed was measured using a handheld device that determined the correct blower input voltage. This voltage correlated to the test speed of 40 km/hr (Meyer et al. 2011). Three replicate samples were placed side-by-side downstream of the blower fan in the center of the wind tunnel. Spires were constructed in front of the pans to disperse wind flow. This was done to try to account for uneven wind erosion (Meyer et al. 2011). Samples were then subjected to a 40 km/hr wind for 3 minutes. Immediately before the wind tunnel was activated, a dust detector was turned on to measure the density (mg/m^3) of emitted particulates less than $10 \mu\text{m}$ in size. Air sampling tubes were placed downstream above the pans, in an attempt to determine the specific aerosol production rate ($\text{mg}/\text{m}^3/\text{s}/\text{m}^2$). Samples were wind tunnel tested at intervals of 1, 2, 4, 7, and 14 days after the bacterial treatment to see the effect of MICP

treatment over time on mass loss (Meyer et al. 2011).

Based upon the test results, Meyer saw that specific concentrations of bacteria and volumes of solution resulted in the lowest amount of mass lost during the tests. Figures 4a and 4b below show the test results.

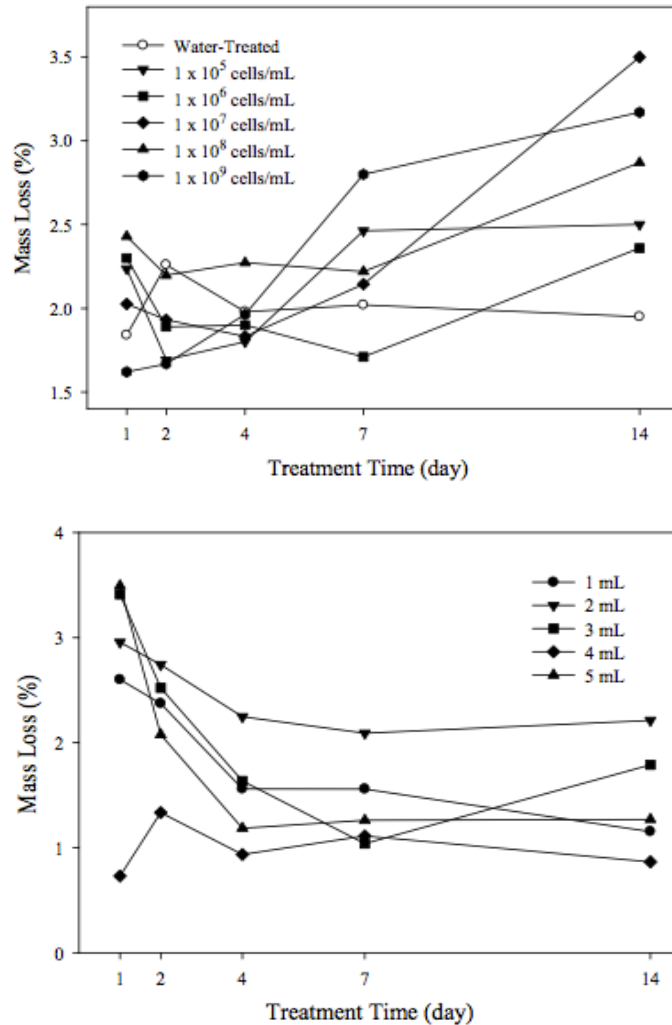


Figure 4a: Percent mass lost at different bacteria concentrations (Meyer et al. 2011)

Figure 4b: Percent mass lost at different solution volumes (Meyer et al. 2011)

From Meyer's test results we can see that the greatest impact of MICP on mass loss and aerosol production rate occurs in high temperature and low humidity environments, similar to arid deserts. This data is shown in Figure 5.

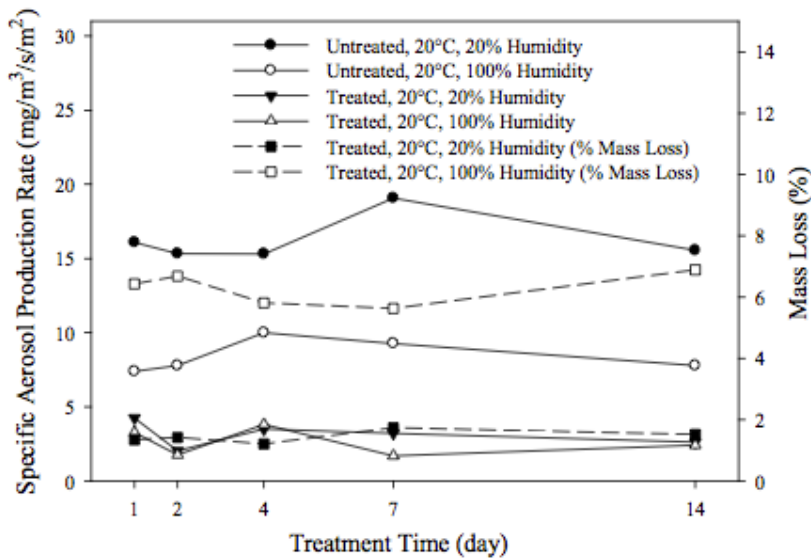


Figure 5: SAPR & Mass loss of treated samples, untreated samples, and different temperature and humidity conditions (Meyer et al. 2011)

There were differences in the mass loss among the washed soils and the unwashed soils and there was a significant increase in cementation in the washed soils. Meyer et al. (2011) speculated that the removal of the finer particles allowed for more carbonate precipitation in the voids of the specimen. Meyer's data show that MICP can be an effective option for dust control.

2.6 Enzyme-Induced Carbonate Precipitation (EICP) Based Studies

Urease enzyme can come from plants as well as microbes. The plant based urease used in previous EICP experiments at ASU use urease from the Jack bean. The Jack bean, also known as the Chickasaw Lima bean, is a common drought resistant bean grown in many areas around the south central U.S. (USDA, 2013). The plant based enzyme offers several advantages to the microbially based enzyme. The first is that there is no need to grow and sustain microbes. There is better utilization of substrates with a plant based enzyme. The microbes producing the urease enzyme use the carbon in the urea hydrolysis reaction as a food source. This will somewhat limit the total effective carbon that is going to production of carbonate. Plant based urease is also applicable to much finer soils. The enzyme is approximately 12 nm x 12 nm. Plant based urease is

readily available for purchase and will degrade after use. Microbially based urease production will leave the organisms behind. The urease enzyme that is extracted from these beans is expensive when purchased from lab supply (the cost of mass produced urease is unknown), but lab grade enzyme is very effective.

Previous erosion control research at ASU was similar to the research at SDSMT, but the ASU research used plant based urease for EICP (Hamdan, Kavazanjian, 2013). The ASU research involved creating 13 samples of native Arizona silty sand. The tests were performed to compare the effect of solution concentration against bare soil and wetted soil (Hamdan and Kavazanjian, 2013). Calcium chloride/urea solutions of 0.3 M, 1 M, and 2 M concentrations were employed in the tests. The tests employed the ASU/NASA Planetary Wind Tunnel. This wind tunnel was designed specifically to test for wind erosion. This wind tunnel creates truly laminar flow over the soil samples. The tests were run differently from the tests done by Meyer et al. (2011). Instead of holding the wind velocity constant, the wind speed was increased incrementally until there was visual detachment of soil particles. The results from these tests are shown in Figure 6.

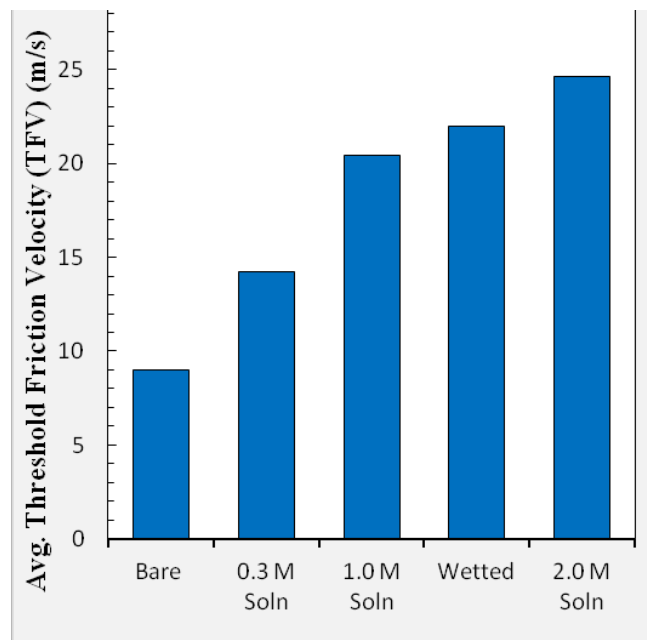


Figure 6: TFV for Cemented Particle Lift off for Different Concentrations (Personal Communication: Nasser Hamdan, ASU)

2.7 Potential Limitations of EICP

There are still many factors concerning the use of carbonate precipitation for dust control that require investigation. Appropriate concentrations, the durability of the process, resistance to surface water and the influence of the treatment on the magnitude of surface water runoff all need to be addressed. Of particular importance are the environmental concerns involved with hydrolysis of urea. Ammonium (NH_4^+) and ammonia (NH_3) are by-products of bio-cementation. Ammonium is potentially harmful if it were to leach in the water supply. Ammonia has a strong odor. The fate and transport of the ammonium must be addressed as well as the odor due to ammonia.

CHAPTER 3

Experimentation Plan

3.1 Introduction

Our goal for our research was to determine the relationship between the concentration of calcium chloride (CaCl_2), urea, and urease enzyme (the cementation solution) used to induce carbonate precipitation at the soil surface and wind erosion resistance for typical wind erosion prone soils. We felt that this was the necessary step forward in the research on this topic. Understanding the relationship between cementation solution concentration and wind resistance is the first step in making this research a viable technique for erosion control. In our research, we also looked at a few other facets of EICP to try and get a better grasp on what was actually happening. This chapter will take a look at the research plan we laid out, and what soils we tested EICP on.

3.2 Experimentation Plan

The primary objective of our experimentation plan was to find the relationship between the concentration of the cementation solution and erosion resistance. The “optimum” condition we were searching for was one where we would achieve detachment velocities in our soil similar to those of water as a means of cost comparison with the typical method of erosion control on construction sites using a water truck. We also wanted to test several soil types. The soil types we employed in our research are briefly summarized in the following table.

Soil Name	Soil Type	Location
Native Arizona Soil	Silty Sand (SM)	Maricopa County, AZ
F60	Uniform Fine Grain Sand (SP)	Purchased
Mine Tailings	Silty Sand (SP-SM)	Southern Arizona Mine

Table 1: Soils used in experimentation

A full description of these soils will be given later in this chapter. When research started, we did not have the Mine Tailings available to us, so we started our research by making testing Native Arizona Soil and F60 sand. These soils were tested in the ASU/NASA Planetary Wind Tunnel. It is a large laminar flow wind tunnel on the campus of ASU that is used to simulate soil erosion. It was built by the college of planetary studies at ASU to simulate soil wind erosion on other planets.

We started our research with two concentrations: 1 M and 2 M solutions of calcium chloride and urea. Pie pans were filled level to the top with the test soil and sprayed with a calcium chloride, urea, and urease solution. We also had three types of control pans for each soil: bare soil with no treatment, a pan sprayed with just water, and a pan for each calcium chloride/urea concentration that had no enzyme applied with it. Thus there were a total of 12 pans, 6 for each soil type, in the initial test program. The pans were sprayed with cementation in the laboratory. We then waited a week before testing. We chose to wait a week because we were unsure as to how long it took the precipitation reaction to occur. After running our first set of pans in the wind tunnel, we made some positive findings. We saw that EICP was effective at reducing fugitive dust and that at the concentration we applied the treated soil was able to withstand the full force of the wind tunnel without detachment. The lack of detachment was an issue that needed to be addressed in the next round of testing. To address this issue, we chose to spray our first set of mine tailing pans with lower concentrations of calcium chloride (CaCl_2), urea, and urease. Eight (8) pans with mine tailings were prepared. However, the concentrations we used were still too high.

In the next round of testing we used even lower concentrations of the EICP solution. In this next round we prepared 9 pans for each soil. We used three different concentrations to create a spectrum of detachment velocities. We also conducted repeatability study by preparing several pans with same concentration to determine the repeatability of our results.

In addition to the wind tunnel testing, we also wanted to do evaluate the strength and durability of the soil crusts, to demonstrate that we really had carbonate precipitation, to look at the precipitated carbonate on a microscopic level, and to test the effects of surface water flow on the treated soil. In order to accomplish these tasks, we retained

crust samples from all treated pans. Multiple samples were taken from each pan. The thickness of all crust samples was measured in to see the variance in cementation penetration depth for different samples. Crust samples were also sent to the Scanning Electron Microscope (SEM) to produce visual images of the carbonate being produced. Finally we used a water erosion kit to see the effects of surface water flow on a treated surface.

3.3 Soils used in Testing

Three different soil materials were employed in the research program: Native Arizona Silty Sand from Southern Maricopa County Arizona, Ottawa F60 Crystal Silica Sand from US Silica Company's Ottawa, Illinois, source, and mine tailings from a mine in southeast Arizona. The soils are referred to herein as Ottawa F60 (or just F60) sand, native Arizona soil, or mine tailings. We chose three different soils because we wanted to see how EICP treatment worked on a variety of different types of soils.

3.3.1 Native Arizona Soil

The native Arizona soil was taken from a residence in Scottsdale Arizona. It is typical native Arizona silty sand. However, for this research, we decided to process the soil so that it didn't have gravel particles or very small clay particles. The large particles (particles retained on the #40 sieve) weren't necessary for testing because they are not the particles that are causing fugitive dust. The small clay particles (particles passing the #325 sieve) were left out because we did not want a plastic soil with cohesion that inhibited wind erosion. It would also reduce the likelihood that there was apparent cohesion, or capillarity, contributing to the strength of the treated specimens. In removing these clay particles, we created a silty sand that was susceptible to fugitive dust. The classification of the native soil was determined in the ASU Geotechnical Engineering Lab by performing grain size distribution (ASTM D 422-63) and Atterberg limits (ASTM D 4318-05) tests. These properties are shown in Table 2. From these properties we determined the soil to be a silty sand with a Unified Soil Classification System (USCS) classification of SM, and an American Association of State Highway and Transportation

Officials (AASHTO) classification of A-2-6. Figure 7 shows the grain size distribution for our processed native soil.

Parameter	Value
D ₆₀	.41
D ₃₀	.055
D ₁₀	.03
C _u	13.3
C _c	.25
LL	26%
PI	0 (NP)
USCS Classification	SM

Table 2: Processed Native Soil Properties

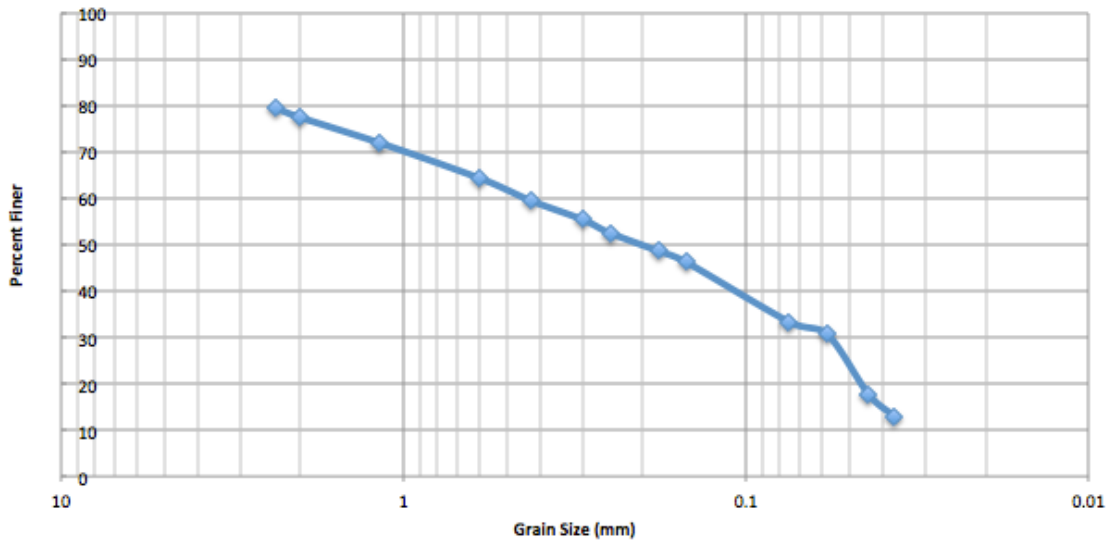


Figure 7: Grain Size Distribution for Processed Native Soil

3.3.2 Ottawa F60 Sand

Ottawa F60 Crystal Silica sand from Ottawa, Illinois was purchased from the US Silica Company. F60 sand consists of white, round sand particles that are 99.8% quartz (US Silica Company 2011). The mean grain size of F60 sand is 0.25 mm. Figure 8 shows

the grain size distribution for Ottawa F60. F60 sand has a USCS classification of SP. Table 3 shows the maximum and minimum void ratios, determined according to ASTM D4254, along with selected physical properties of F60 sand. These properties of the F60 sand can be found in Appendix A.

PARAMETER	VALUE
e_{\max}	.8315
e_{\min}	.6014
D_{10}	.15 mm
D_{30}	.19 mm
D_{50}	.23 mm
D_{60}	.26 mm
C_u	1.73
C_c	.926
G_s	2.65

Table 3: F60 sand Properties (Gutierrez, 2013)

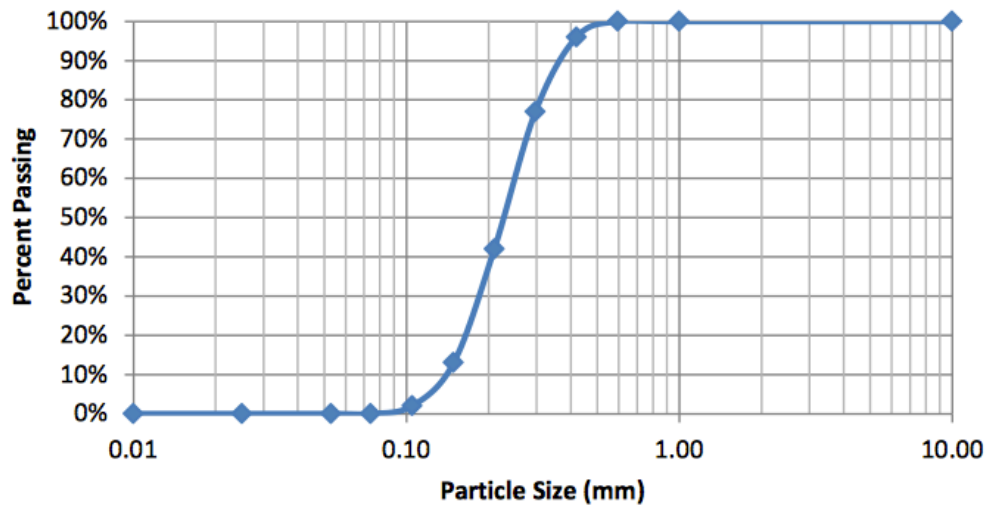


Figure 8: F60 Grain Size Distribution (Gutierrez, 2013)

3.3.3 Mine Tailings

The third soil we used for this research came from a mine tailings pile in southern Arizona. Mine tailings are the remnants from the copper mining process. Mine tailings are mostly pulverized or chemically broken down rock. The current practice is to spread these mine tailings in large piles that are a significant source of dust generation. The mine tailings became the soil of choice for supplementary testing after our initial wind tunnel testing. The properties of the mine tailings are shown in Table 4 below. We conducted grain size distribution (ASTM D 422-63) and Atterberg limits (ASTM D 4318-05) tests to classify the mine tailings. The resulting USCS soil classification was SW-SM, or fine to coarse silty sand. The mine tailings had an AASHTO classification of A-2-6. The grain size distribution of the mine tailings is shown in Figure 9.

Parameter	Value
D ₆₀	.29
D ₃₀	.17
D ₁₀	.083
C _U	3.49
C _C	1.2
LL	29%
PI	0 (NP)
USCS Classification	SW-SM

Table 4: Mine Tailing Properties

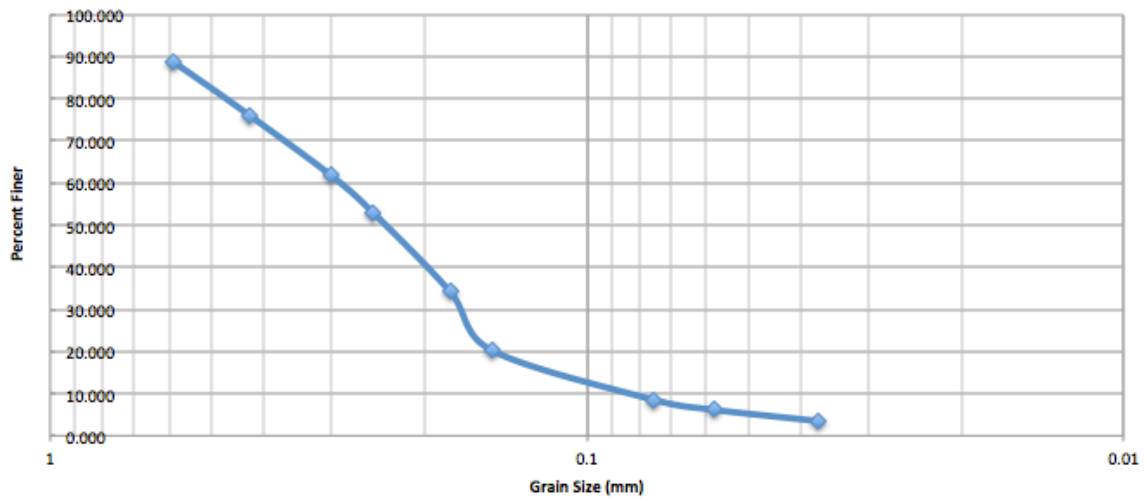


Figure 9: Grain Size Distribution: Mine Tailings

CHAPTER 4

Wind Tunnel Testing

4.1 NASA/ASU Planetary Wind Tunnel

We employed the NASA/ASU Planetary wind tunnel (ASUWIT) for this project. This wind tunnel was designed to create a laminar flow for measuring wind detachment velocity for soil erosion experiments. The wind tunnel is part of the Planetary Aeolian Laboratory (PAL) at ASU. PAL is associated with NASA's Planetary Geology and Geophysics program. It is a unique facility used for conducting experiments and simulations of Aeolian processes (windblown particles) under different planetary atmospheric environments.

The ASUWIT is a 13.7-m long, 0.7 m high, 1.2 m wide open circuit boundary-layer wind tunnel that operates under ambient temperature and pressure conditions and is capable of wind speeds of 30 m/sec (Williams, 2013). Air is pulled through the tunnel by a large fan mounted in the downwind section of the tunnel. A viewing area of the test bed is encased by plexiglass with doors to access the test section for the setup of experiment (Williams, 2013). The ASUWIT facility can measure wind speed, temperature and humidity inside the tunnel. Physical conditions in the room outside of the tunnel are also monitored. These data include laboratory temperature, humidity and barometric pressure (Williams, 2013.) Wind conditions exterior to the building, including wind direction and speed, are also recorded. Independent sources power the pressure transducers, humidity sensors, anemometers, and wind vanes (Williams, 2013). The following images are all of the ASUWIT.



Figure 10: ASU/NASA Planetary Wind Tunnel.

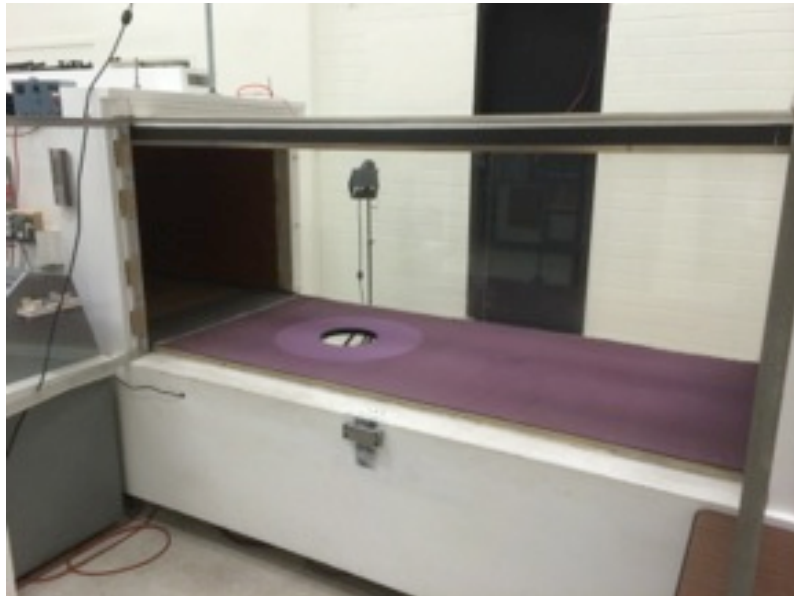


Figure 11: Wind Tunnel Viewing Window.



Figure 12: Rear Fan of Wind Tunnel.

4.2 Wind Tunnel Tests (Round 1)

The first round of wind tunnel tests involved testing all three soils (native silty sand, mine tailings, and F60). We tested the native soil and the F60 soil using solutions of calcium chloride and urea at 1 M and 2 M concentrations with enzyme included. We also tested control pans of just calcium chloride and urea with no enzyme because this is already a practice of erosion control. Note that we refer to the concentration of each solution by the concentration of calcium chloride in each solution. We did one test at 1 M concentration and two tests at 2 M concentration because we wanted to see if we could get the same results twice with the 2 M solution. We also tested all three soils with no treatment and treated with just water.

We sprayed the specimens with water in order to compare the wetted detachment velocities versus the treated soil pans. The pans sprayed with enzyme, calcium chloride, and urea, were allowed to sit for one week before we tested them in the wind tunnel. The waiting period was done to allow completion of the urea hydrolysis reaction. Since we wanted the control specimens and the enzyme treated specimens to be given the same treatment, they were also allowed to cure for 7 days. The wetted samples however, were sprayed with spray bottles right before they were placed in the wind tunnel in order to reflect the performance of a soil that has just been wetted in the field. For the first round of tests we chose initial application concentrations of 1 M and 2 M as an estimate of what

we thought would be an effective concentration. However, after the initial tests of the native soil and F60 soil, we determined 1 M to be too high to achieve our objective of an erosion resistance similar to that of wetted soil and we decided to lower the concentrations to 0.375 and 0.75 M for our first set of mine tailings tests.

4.2.1 Pie Pan Preparation

Pie Pans were created in a consistent manner to try and make the soils in the pans have a consistent density (i.e. the same density for pans of the same soil type). We used 9-inch diameter pie pans for these experiments. These pans were fit within a holding ring on the wind tunnel. The depth of the pans was about 1 in. Pan weight was measured prior to filling. Soil was then scooped into the pans, and densified through various methods. Densification methods included tapping on the side of the pans (typically 3 taps for every $\frac{1}{4}$ turn), lifting and dropping the pan, and tapping the top with a flat edge in order to break up soil chunks that would otherwise keep our soil pans from being smooth. We tried to make the pans denser as research progressed because we noticed we were getting soil settlement during transport. Also each soil behaved differently as it was being added to the pan, so we had to adjust our methods for each soil. For the native soil we used the following procedure.

Native Arizona Soil

- 10 Scoops of Soil
- Densified with 3 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- 3 Scoops of Soil
- Densified with 3 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Scraped excess soil of the pan

For the native Arizona soil, we achieved what we considered to be reasonably similar densities using this procedure, as shown in Table 5.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
1	1744.10	1.25	77.83
2	1781.80	1.27	79.51
3	1712.50	1.22	76.42
4	1739.00	1.24	77.59
5	1698.00	1.21	75.77
11	1750.10	1.25	78.09

Table 5: Pan Densities for Native Arizona Soil

When preparing the pans of F60 sand, the soil was very easy to pour compared to the native soil. The fact that it was a clean sand made a big difference in ease of placement because it flowed and smoothed easily. The typical preparation method for F60 was as follows.

F60 Medium to Fine Grain Silica Sand

- 10 Scoops of Soil
- Densified with 3 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- 10 Scoops of Soil
- Densified with 3 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- 3 Scoops of Soil
- Evened with a flat edge ruler
- Scraped excess soil of the pan

With the F60 pans we achieved densities that seem to be much higher than a typical in-situ density. However, we still had some minor settlement, around a few millimeters, at the surface after transporting the pans to the wind tunnel. The densities are shown in Table 6.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
6	2188.7	1.56	97.68
7	2214	1.58	98.81
8	2226.9	1.59	99.38
9	2214.8	1.58	98.84
10	2233.2	1.60	99.66
12	2187.5	1.56	97.62

Table 6: Pan Densities for F60 Sand.

Preparation of the mine tailings specimens was by far the most difficult for our three soil types. The tailings contained many small clumps of soil. This is due to the fine content in the soil holding some moisture, which creates capillary suction that holds clumps of fines together. These clumps of soil made it very difficult to make an even surface on the pan. Specimen preparation for the mine tailings involved breaking up of clumps and more densification effort relative to the other two soil types. The typical preparation method for the mine tailings is as follows.

Mine Tailings

- 5 Scoops of soil
- Densified with 10 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Broke up soil clumps
- 5 Scoops of soil
- Broke up soil clumps
- Densified with 10 spoon taps for each quarter turn of the pan
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Densified with 10 spoon taps for each quarter turn of the pan
- Lifted and dropped the pan 6 times
- Tapped on pan and tamped soil clumps to even soil with a flat edge ruler
- Scraped excess soil of the pan.

This method of preparation did take longer than the other pans, but we also achieved high enough densities to remove surface settlement during pan transportation. The densities are shown in Table 7.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
13	1907.30	1.36	85.10
14	1903.00	1.35	84.92
15	1968.30	1.40	87.83
16	1869.60	1.34	83.42
17	1946.40	1.39	86.85
18	1988.70	1.42	88.74
19	1949.30	1.39	86.98
20	1960.10	1.40	87.46

Table 7: Pan Densities for Mine Tailings

4.2.2 EICP Solution Formulation

After specimen preparation, we were ready to apply the EICP solutions. Our initial plan was to apply two separate solutions to precipitate carbonate on top of the soil in the pans. One solution contained calcium chloride and urea, while the other solution contained urease enzyme and a dried milk stabilizer. The solutions were mixed separately because urea hydrolysis occurs as soon as urease enters solution with calcium chloride and urea. The stabilizer was used in order to let the enzyme reach its full potential as a catalyst. Stabilizers help preserve enzyme activity and structural integrity by preventing nonspecific adsorption of the enzyme onto substrates and preventing denaturation in ionic fluids (Zhao, 2010). Non-fat dry milk is a good stabilizer because it has stable glycoproteins that coordinate (not bond) with the enzyme and do not interfere with the enzyme's active site.

For our calcium chloride and urea solution, we chose to keep the ratio between calcium chloride and urea at 2 parts calcium chloride to 3 parts urea. We felt that this

would be an effective ratio for EICP. The reason why we chose to use this ratio is based on stoichiometry. Having more urea in solution will yield a higher amount of base. We felt that by having more base (OH⁻) we were creating better conditions for EICP to occur. One could argue that having a higher level of calcium chloride would be better because it would increase our saturation index. Having a higher saturation index (value greater than 1 cause precipitation) would allow us to precipitate more calcium chloride. However, at higher pH values the saturation index will decrease thus making it easier to achieve values higher than 1. So by increasing the amount of Urea over calcium chloride could solve both arguments, and is thus the ratio we chose. Pans 1-12 contained native soil and F60 soil. The solution preparations for pans 1-12 was as follows.

For Pans 1-12

Based on previous work at ASU, the first set of tests was conducted using concentrations of 2 M and 1 M for our calcium chloride solutions. To save time on mixing, we made a large amount of 2 M solution and then diluted part of that solution to create the 1 M concentration.

Solution 1: 900 ml @ 2 M CaCl₂ and 3 M Urea

$$CaCl_2 = 2 \frac{mol}{l} * 147.01 \frac{g}{mol} * 0.9 l = 264.619 \text{ grams of } CaCl_2$$

$$Urea = 3 \frac{mol}{l} * 60.06 \frac{g}{mol} * 0.9 l = 162.16 \text{ grams of } CaCl_2$$

600 ml of the solution above was enough to spray the 2 M pans. We used the remaining 300 ml to create the 1 M solution.

$$300 \text{ ml @ } 2M \text{ conc.} + 300 \text{ ml of water} = 600 \text{ ml @ } 1M \text{ conc.}$$

After creating these two solutions, we needed to adjust the pH of our solutions to provide the proper conditions to induce EICP. We wanted a solution pH between 7.5 and 9.5 because this is the pH range most amenable to calcium carbonate (CaCO₃) precipitation.

The pH was adjusted by adding sodium hydroxide (NaOH) to the calcium chloride/urea solution, and the changes were checked with a pH probe. The final pH of our solutions after adjustment were:

- pH of 2M CaCl₂ Solution: 8.3
- pH of 1M CaCl₂ Solution: 7.8

For the enzyme solution, the calculations are slightly easier. Based upon previous work at ASU, our desired concentration of enzyme was 0.5 grams/liter and our desired concentration of milk was 4 grams/liter. So, to create 1 liter of solution we used the following amounts of urease and dry milk:

$$\text{Urease} = 0.5 \frac{\text{g}}{\text{l}} * .2 \text{ l} = 0.108 \text{ grams of Urease}$$

$$\text{Dry Milk} = 4 \frac{\text{g}}{\text{l}} * .2 \text{ l} = 0.84 \text{ grams of Dry Milk}$$

For Pans 13-20

After testing pans 1-12, we decided we had to lower our concentrations for the next batch of tests. Since we already had calcium chloride and urea solution in the lab at 1.5 M calcium chloride, we decided to cut this solution in half and use a 0.75 M calcium chloride solution with the mine tailings. We also decided to cut this solution in half again and also use a concentration of 0.375 M calcium chloride in the testing.

Original Solution: 500 ml @ 1.5 M CaCl₂ and 1.875 M Urea

Solution #1: 200 ml of the solution was poured into a separate container. We then added 200 ml of water to get 400 ml of a solution at final concentration of 0.75 M calcium chloride.

Solution #2: I took 100 ml of the original solution and added 300 ml of water to create a 400 ml of solution at a concentration of 0.375 M calcium chloride.

After creating these two solutions, we again needed to adjust the pH of our solutions to facilitate EICP. After adjustment the following pH values were achieved:

- pH of 0.75 M CaCl₂ Solution: 8.6
- pH of 0.375 M CaCl₂ Solution: 8.4

One liter of solution at the desired concentration of enzyme of 0.5 grams/liter for urease and 4 grams/liter of dry milk were achieved as follows:

$$\text{Urease} = 0.5 \frac{\text{g}}{\text{l}} * .1 \text{ l} = 0.055 \text{ grams of Urease}$$

$$\text{Dry Milk} = 4 \frac{\text{g}}{\text{l}} * .1 \text{ l} = 0.403 \text{ grams of Dry Milk}$$

4.2.3 Pie Pan Spray Application

Our initial plan was to apply two separate solutions, one of calcium chloride and urea and one of urease and dry milk, to our soil pans. There were a few reasons as why we chose to use two separate solutions. Urease enzyme is the catalyst that enables the process of urea hydrolysis. This rate at which urease catalyzes the reaction is an issue for our application technique because the reaction happens so fast: calcium carbonate will begin to precipitate instantly when the calcium chloride, urea, and urease enzyme are brought together. We were concerned that by mixing everything together before applying it to the soil we not only were losing some carbonate precipitation (because it would happen in the mixing vessel) but we were also at risk of plugging our sprayers. We felt that by applying the urease after applying the calcium chloride and urea solution we would not lose any cementation. Hopefully, all of the reaction would occur at the surface of the soil. So we initially proceeded by spraying the two separate solutions simultaneously on the soil.

After we decided on an application method, we needed to figure out how to accurately spray the desired rates onto the soil pans. An automated spray pump system was not available to us, so application of the solutions was conducted with hand sprayers. While hand sprayers are suitable for applying the small volumes used in this work, it is difficult to maintain a constant and precise spray pattern among the pans. In order to spray the correct volume of solution on each pan, we made markings on our spray bottles for each 200 or 100 ml of solution, depending on which concentration of solution was being applied. In order to create the markings, we filled the bottles with the appropriate increments of water measured using graduated cylinders.

Pans were spread out on tables for spray application. We sprayed our entire volume of calcium chloride solution and enzyme solution simultaneously on a pan before moving on to the next pan. This first set of specimens was sprayed with an application volume of 150 ml of calcium chloride/urea solution, and 25 ml of enzyme solution. This gave us a rate around 24 l/m² for the calcium chloride/urea solution and around 4 l/m² for the enzyme solution. Initially, it seemed as if we were losing some spray volume around the pan. Therefore, after the first few pans we used a protective plastic shield around each pan as we sprayed. This shield was a flat plastic sheet that was made to fit around the circumference of the pan via a heating torch.

During the physical spraying of the pans we ran into an issue with our spray volumes. The markings we had worked well until you reached the final few ml of solution. At that point, we lost prime in our pumps and were not able to get out the rest of the solution. We lived with this problem for the firsts set of pans and resolved to address it in the future. The following figures show the spray technique used, as well as what the final product of each pan looked like.

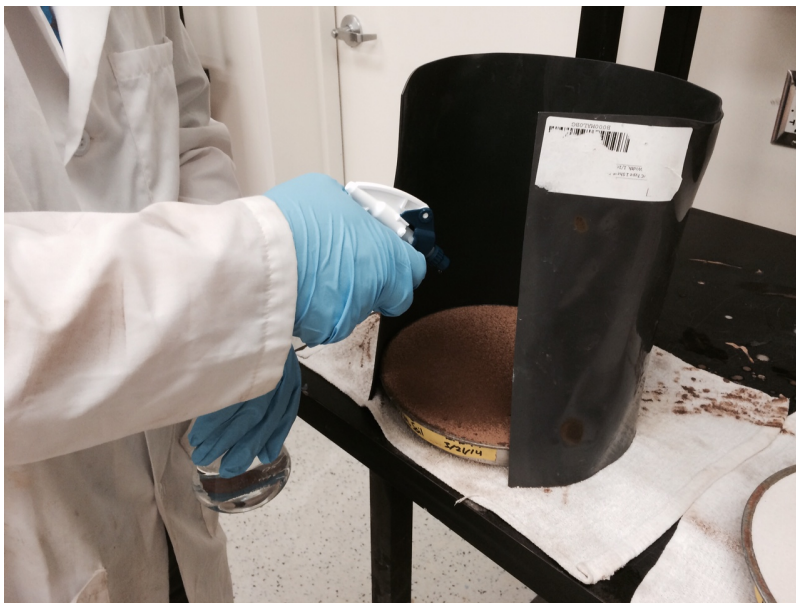


Figure 13: Spray Application Method



Figure 14: F60 soil pan sprayed with CaCl_2 and Urease Solutions



Figure 15: F60 and Native Soil Pans Post Spray Application

4.2.4 Wind Tunnel Tests & Results

After pans were sprayed and allowed to sit for a week, specimens were ready for testing in the wind tunnel. The prepared specimens were transported to the wind tunnel facility and placed in the retainer ring in the bed of the wind tunnel.

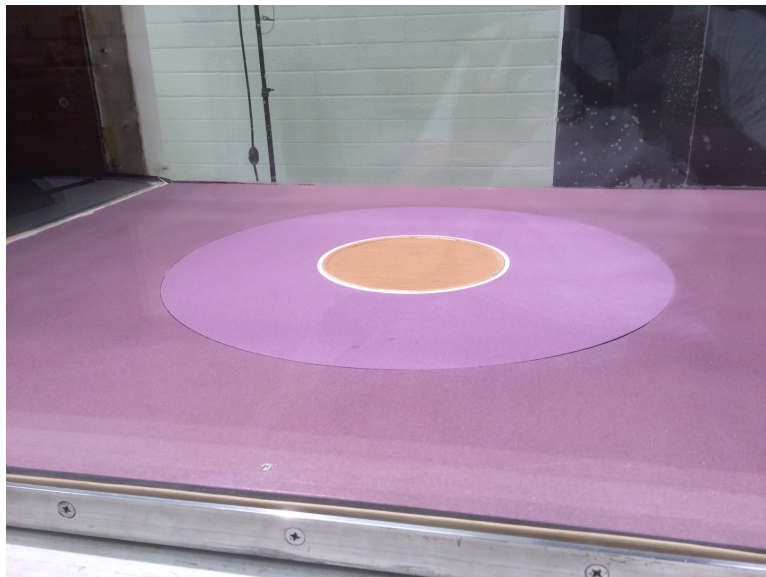


Figure 16: Soil Specimen Prior to Testing

After placing the specimen in the wind tunnel, the wind velocity was started at a low speed and slowly and steadily increased until there was visual detachment of soil from the surface of the pan. Note that at the start of the test we typically saw an initial “dusting” of soil particles leaving the surface of the pan. This initial dusting was not considered detachment because it was a minimal amount of particles that we deemed as being loosened during transport. Detachment occurred when a piece of soil crust broke away from the surface. The process worked better when there were two sets of eyes watching each pan. The Wind Tunnel had a maximum velocity of 30 m/s. However, we ran the risk of having the soil pans sucked into the wind tunnel at that speed. This caused us to stop testing at 25 m/s.

Native Arizona Soil

Pans 1-6 were native soil. We started out these tests at a velocity of 3 m/s. We saw detachment of untreated soil at around 8 m/s. When treated with a control solution of just calcium chloride and urea the detachment velocity was 14.5 m/s. When untreated soil was thoroughly wetted, the detachment velocity was 22 m/s. We reached the maximum test velocity of 25 m/s without any visible detachment. The results are presented in Table 8 and Figure 17.

Native Soil (Round 1)			
Pan #	Erosion control Method	Avg. DV (m/s)	Avg. DV (mph)
1	Bare Soil	8.0	17.9
2	Water	22.0	49.21
3	1 M Control	14.5	32.44
4	1 M + Enzyme	> 25.0	55.92
5	2 M + Enzyme	> 25.0	> 55.92
11	2 M + Enzyme	> 25.0	> 55.92

Table 8: Native Soil Wind Tunnel Results at 24 l/m²

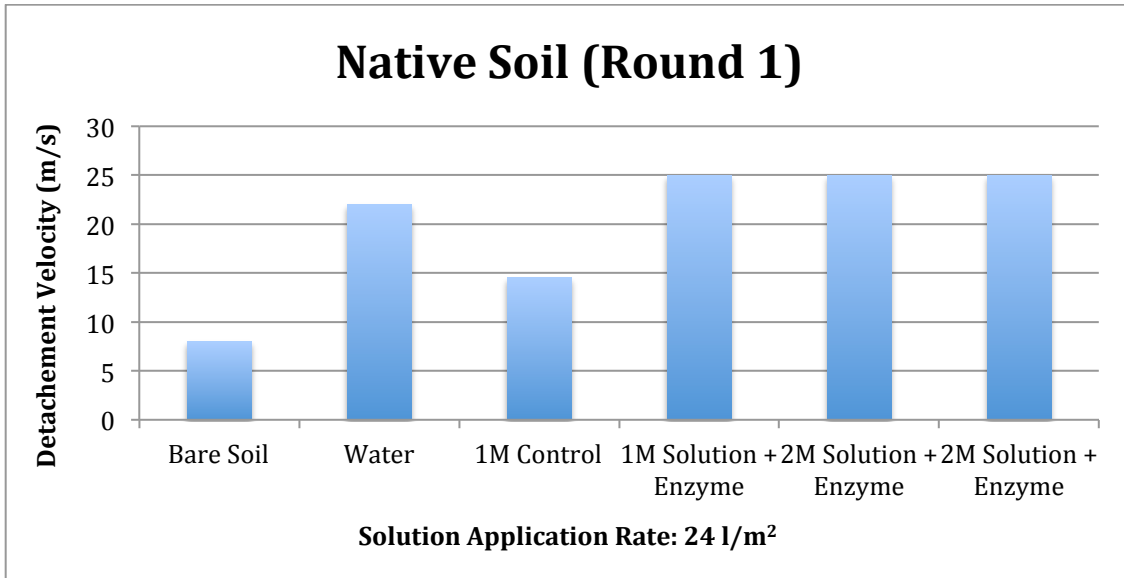


Figure 17: Native Soil Wind Tunnel Results

Note that the enzyme stabilized soil in this round of testing reached the maximum wind tunnel velocity of 25 m/s without detachment.

F60 Sand

We started out this test at a velocity of 3 m/s. When we ran our first pan, we saw detachment of untreated soil at around 8.5 m/s. When treated with a control solution of just calcium chloride and urea the detachment velocity was 23 m/s. When untreated soil was thoroughly wetted, the detachment velocity was 23 m/s. We reached the maximum test velocity of 25 m/s without any visible detachment. The results are shown in the following table and figure.

F60 (Round 1)			
Pan #	Erosion control Method	Avg. DV (m/s)	Avg. DV (mph)
6	Bare Soil	8.5	19.01
7	Water	23.0	51.45
8	1 M Control	23.0	51.45
9	1 M + Enzyme	>25.0	>55.92
10	2 M + Enzyme	>25.0	>55.92
12	2 M + Enzyme	>25.0	>55.92

Table 9: F60 Sand Wind Tunnel Results at 24 l/m²

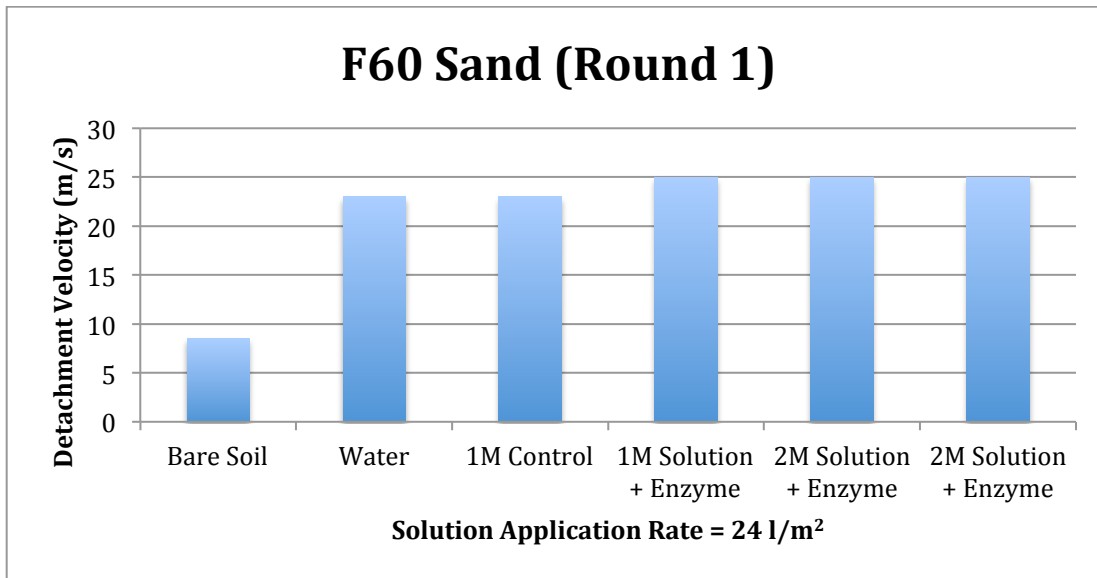


Figure 18: F60 Sand Wind Tunnel Results

Note that the enzyme stabilized soil in this round of testing reached the maximum wind tunnel velocity of 25 m/s without detachment.

Mine Tailings

We started out this test at a velocity of 3 m/s. When we ran our first pan, we saw detachment of untreated soil at around 7 m/s. When treated with a control solution of just calcium chloride and urea the detachment velocity was 19.5 m/s with a 0.375 M solution and 16 m/s with a 0.75 M solution. When untreated soil was thoroughly wetted, the detachment velocity was 23 m/s. We reached the maximum test velocity of 25 m/s without any visible detachment for the 0.75 M solution. With the 0.375 M solution we reached a detachment velocity of 23 m/s. The results are shown in the following table10 and Figure 19.

Mine Tailings (Round 1)			
Pan #	Erosion control Method	Avg. DV (m/s)	Avg. DV (mph)
13	Bare Soil	7.0	15.66
14	Water	23.0	51.45
15	0.375M Control	19.5	43.62
16	0.75M Control	16.0	35.79
17	0.375M + Enzyme	23.0	51.45
19	0.75M + Enzyme	>25.0	>55.92

Table 10: Mine Tailing Wind Tunnel Results at 24 l/m²

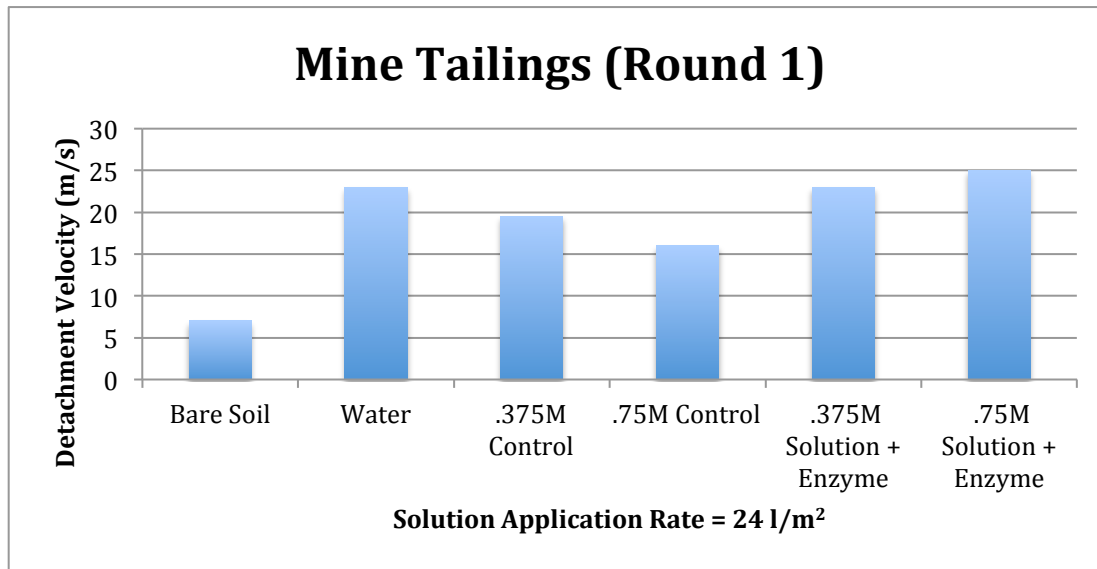


Figure 19: Mine Tailing Wind Tunnel Results

Note that we see that we have weaker crust strength for the 0.75 M control solution relative to the 0.375. The 0.375 M solution reached the maximum wind tunnel velocity of 25 m/s.

Combined Results

The combined results of the first 20 tests are presented in Figure 20.

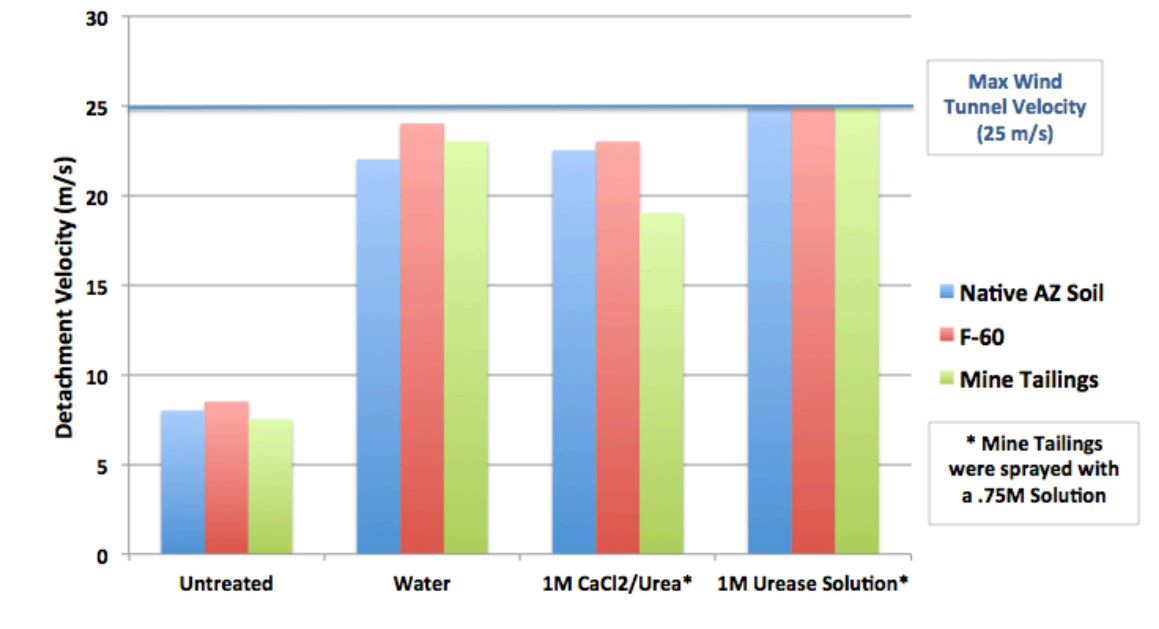


Figure 20: Combined Results for Round One of Wind Tunnel Testing

4.2.5 Lessons Learned (Round 1)

Several important lessons were learned from round one of wind tunnel testing. We have shown that EICP can work as a method of fugitive dust mitigation. We created strong soil crusts capable of withstanding wind velocities that beat the “gold standard” of thoroughly wetting soil for dust control. However, there are multiple issues that still need to be addressed. Since the soil pans cemented with enzyme were able to withstand the maximum wind tunnel velocity, we have no numerical values for crust wind resistance. There is also the question of how much carbonate is actually present in the soil. The calcium chloride alone can act as a control agent to prevent fugitive dust. The control tests using only the calcium chloride solution showed substantial wind erosion resistance. In these control tests, salt may precipitate in the pore space and at grain contacts, causing a crust to form. So, additional testing was needed using much lower concentrations of calcium chloride and urea and there needed to be more investigation into the issue of salt stabilization.

4.3 Wind Tunnel Tests (Round 2)

4.3.1 Pie Pan Preparation

In Round 2 of wind tunnel testing, we resolved that the unit weight of the soil in the pans needed to increase to reduce settlement that occurred during the transport of the soil pans. Again, each soil behaved differently as it was being added to the pan, so we had to adjust our preparation methods for each soil. We started round two of testing by looking at the mine tailings again. The mine tailings still proved to be the most difficult soil to work with. The tailings contained many small clumps of soil. These clumps of soil made it very difficult to make an even surface on the pan. So preparation of mine tailings specimens involved more densification and breaking up of clumps relative to the other two soil types. The typical preparation methods used in Round 2 of wind tunnel testing were as follows.

Mine Tailings

- 5 Scoops of soil
- Densified with 5 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Broke up soil clumps
- 5 Scoops of soil
- Broke up soil clumps
- Densified with 5 spoon taps for each quarter turn of the pan
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Scraped excess soil of the pan.

The densities for the mine tailings in our second round of testing ended up being lower than the densities in our original pans. This was not intended, however we still achieved densities high enough to minimize settlement during transportation. The densities of the

nine mine tailings specimens prepared for Round 2 wind tunnel testing are shown in Table 11.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
22	1758.6	1.26	78.47
23	1758.9	1.26	78.49
24	1785.6	1.28	79.68
25	1941.5	1.39	86.64
26	1726.2	1.23	77.03
27	1749.8	1.25	78.08
28	1971.9	1.41	87.99
29	1786	1.28	79.70
30	1800	1.29	80.32

Table 11: Pan Densities for Mine Tailings

The F60 sand was very easy to pour and thus F60 specimens were easy to create compared to the mine tailings. The fact that it was a clean sand made a big difference in ease of placement because it flowed and smoothed easily. The typical preparation method for F60 is as follows.

F60 Medium to Fine Grain Silica Sand

- 10 Scoops of Soil
- Densified with spoon 5 taps for each quarter turn of the pan
- Lifted pan and dropped it 3 times
- Evened with a flat edge ruler
- 10 Scoops of Soil
- Densified with spoon 5 taps for each quarter turn of the pan

- Evened with a flat edge ruler
- 5 Scoops of Soil
- Densified with spoon 5 taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Scraped excess soil of the pan

With the F60 pans we achieved densities that seem to be much higher than a typical in-situ density. The densities of these pans were very similar to the densities of the pans in Round 1. The densities are shown in Table 12.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
31	2213.4	1.58	98.77
32	2177.4	1.56	97.16
33	2185.9	1.56	97.54
34	2198.9	1.57	98.12
35	2195.3	1.57	97.96
36	2190.6	1.56	97.75
37	2201.4	1.57	98.23
38	2194.1	1.57	97.91
39	2210.1	1.58	98.62

Table 12: Pan Densities for F60 Sand.

Native Arizona Soil

- 10 Scoops of Soil
- Densified with 3 spoon taps for each quarter turn of the pan

- Evened with a flat edge ruler
- 3 Scoops of Soil
- Densified with 3 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Densified with 3 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Scraped excess soil of the pan

For the native Arizona soil, we achieved very sporadic densities compared to our original pans. Some pans had a higher density, while others had a lower density. The data is shown in Table 13.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
40	1940	1.39	86.57
41	1910	1.36	85.23
42	1690	1.21	75.41
43	1830	1.31	81.66
44	1850	1.32	82.55
45	1560	1.11	69.61
46	1670	1.19	74.52
47	1650	1.18	73.63
48	1740	1.24	77.64

Table 13: Pan Densities for Native Arizona Soil

4.3.2 EICP Solution Formulation

Since we achieved the maximum wind tunnel velocity without displacement with the treated samples in Round 1 testing, we chose to employ three lower concentrations of calcium chloride - urea solution for each soil type in Round 2 testing. In Round 2, we used 0.2 M, 0.1 M, and 0.05 M calcium chloride solutions. For our calcium chloride and

urea solution, we chose to keep the ratio between calcium chloride and urea unchanged from Round 1 testing. However, we made a change in the enzyme application volume for Round 2. We believed that by employing more volume of enzyme solution at the same concentration we could do a better job of EICP. We felt that this higher volume would be able to wash down some salts while causing more carbonate reaction, thereby create a thicker crust.

Mine tailings testing for Round 2 was done in a similar manner as for Round 1, with two solutions applied separately. Our testing of the native Arizona soil and the F60 soil for Round 2 was done a few weeks after our mine tailing studies for Round 2. We decided to change our application method after the native soil and F60 pans and mix the two solutions together prior to application. This change was based upon the absence of carbonate crystals in scanning electron microscope (SEM) images of the treated soil mine tailings specimens. Solution preparation for Round 2 test specimens was as follows.

For Pans 22-30

To save time on mixing, we made a large amount of 0.2 M solution and then diluted that solution to create the 0.1 M and 0.05 M concentrations.

Solution 1: 800 ml @ 0.2 M Calcium Chloride and 0.3 M Urea

$$CaCl_2 = 0.2 \frac{mol}{l} * 147.01 \frac{g}{mol} * 0.8 l = 23.539 \text{ grams of } CaCl_2$$

$$Urea = 0.3 \frac{mol}{l} * 60.06 \frac{g}{mol} * 0.8 l = 14.421 \text{ grams of } CaCl_2$$

450 ml of the solution above was enough to spray the 0.2 M pans. Therefore, we used 225 ml of the 0.2 M calcium chloride solution to create the .1 M solution.

$$225 \text{ ml @ } 0.2 \text{ M conc.} + 225 \text{ ml of water} = 450 \text{ ml @ } 0.1 \text{ M conc.}$$

We took 112.5 ml of the 0.2 M solution to create the 0.05 M solution.

$$112.5 \text{ ml @ } 0.2 \text{ M conc.} + 337.5 \text{ ml of water} = 450 \text{ ml @ } 0.05 \text{ M conc.}$$

After creating these solutions, we needed to adjust the pH to create the desired conditions to induce EICP. We want a solution pH between 7.5 and 9.5 because the solution is more likely to create calcium carbonate. After adjustment, the following pH values were achieved:

- pH of 0.2 M CaCl₂ Solution: 9.3
- pH of 0.1 M CaCl₂ Solution: 9.2
- pH of 0.05 M CaCl₂ Solution: 9.12

Our concentration of enzyme is 0.5 grams/liter and our concentration of milk is 4 grams/liter. We prepared 0.6 liters of enzyme solution as follows:

$$\text{Urease} = 0.5 \frac{\text{g}}{\text{l}} * .6 \text{ l} = 0.302 \text{ grams of Urease}$$

$$\text{Dry Milk} = 4 \frac{\text{g}}{\text{l}} * .6 \text{ l} = 2.40 \text{ grams of Dry Milk}$$

For Pans 31-48

For pans 31-48 there was a change in how the pans were sprayed. It was decided to apply a single mixture of urease, calcium chloride, and urea instead of two separate solutions. We also increased the rate of enzyme applied in hopes of more carbonate precipitation (as noted previously). These changes affected our solution preparation procedure. We needed to adjust our concentrations to account for the dilution caused when the enzyme solution is added to the calcium chloride and urea solution. We decided to apply 200 ml of solution to each specimen, with 155 ml being calcium chloride solution and 45 ml being urease solution. The following example equation shows how we adjusted the volume of calcium chloride.

$$0.2 \text{ M CaCl}_2 = \left(\frac{155 \text{ ml}}{200 \text{ ml}}\right) (X) \Rightarrow X = 0.26 \text{ M CaCl}_2$$

Solution 1: 1700 ml @ 0.26 M CaCl₂ and 0.39 M Urea

$$\text{CaCl}_2 = 0.26 \frac{\text{mol}}{\text{l}} * 147.01 \frac{\text{g}}{\text{mol}} * 1.7 \text{ l} = 61.166 \text{ grams of CaCl}_2$$

$$\text{Urea} = 0.39 \frac{\text{mol}}{\text{l}} * 60.06 \frac{\text{g}}{\text{mol}} * 1.7 \text{ l} = 37.98 \text{ grams of CaCl}_2$$

930 ml of the solution above will be enough to spray the 0.26 M pans. We then take 465 ml to create the 0.129 M solution.

$$465 \text{ ml @ } 0.26 \text{ M conc.} + 465 \text{ ml of water} = 930 \text{ ml @ } 0.129 \text{ M conc.}$$

We then take 232.5 ml to create the 0.065 M solution.

$$232.5 \text{ ml @ } 0.26 \text{ M conc.} + 697.5 \text{ ml of water} = 930 \text{ ml @ } .065 \text{ M conc.}$$

After creating these two solutions, we needed to adjust the pH of our solutions to establish favorable conditions to induce EICP. We want a solution pH between 7.5 and 9.5 for calcium carbonate (CaCO₃) precipitation.

The adjusted pH of the solutions were as follows:

- pH of 0.26 M CaCl₂ Solution: 8.97
- pH of 0.129 M CaCl₂ Solution: 9.07
- pH of 0.065 M CaCl₂ Solution: 9.15

For the enzyme spray we were using a 2 grams/liter concentration of urease over the entire 200 ml, but we were only adding 45 ml of solution. So we needed to make an adjustment to our urease solution as shown below:

$$(200 \text{ ml of solution}) \left(2 \frac{\text{g}}{\text{l}}\right) = (45 \text{ ml of solution})(X)$$

$$X = 0.88 \frac{\text{g}}{\text{l}}$$

Using our new concentration of 0.88 grams/liter, created a new enzyme solution. We still kept the same concentration of dry milk stabilizer.

$$\text{Urease} = 0.88 \frac{\text{g}}{\text{l}} * 0.540 \text{ l} = 0.4752 \text{ grams of Urease}$$

$$\text{Dry Milk} = 4 \frac{\text{g}}{\text{l}} * 0.540 \text{ l} = 2.16 \text{ grams of Dry Milk}$$

4.3.3 Cementation Solution Spray Applications

The mine tailings were treated with the same spray application method as all the previous pans. We mixed the two solutions of calcium chloride/urea and urease enzyme separately and applied them one after another for EICP. However, we did upgrade on one aspect of our spray technique for the Round 2 mine tailings. Instead of marking spray bottles and struggling with applying the correct volume, we used Erlenmeyer flasks as our chemical solution holders. These flasks had measurement lines on the glassware. In addition, it was much simpler to extract all of the solution from the bottom of the flask because we could move the induction tube around.

We changed the application method for the soil pans of F60 and native Arizona soil for Round 2. The change was made because there was no visible calcium carbonate in our crust samples and there was no odor of ammonia during treatment (ammonia is a by-product of the carbonate precipitation reaction). We therefore decided to make a change in the application method as well as the concentrations of urease enzyme for Round 2 testing of F60 and native soil. We decided to mix the two solutions together and apply it to the soil surface. We washed out the sprayer tip in between each round of application to reduce the potential for clogging the tip. We sprayed 4 pans at a time, applying 50 ml of solution to each pan. So we still applied up 200 ml of solution in each round of spraying. We gave the pans a minute or two in between rounds of solution

application to allow for some cementation to occur. We repeated that process 4 times so that all the pans received the same 200 ml of solution as in previous one-pass treatments.

There are a couple of ways that the precipitation of carbonate can be recognized when you are spraying the pans. The first is by the color of the surface of the pans. If it turns white, then there is a strong indication that carbonate is present. Another is by the odor of the ammonia generated during carbonate precipitation. Carbonate precipitation was also indicated by a white precipitate that started to form in the spray bottle as soon as the two solutions were mixed together. When pans 31-48 were being sprayed, not only did the surface of the pans turn white, but there was a strong odor of ammonia. This gave us confidence that we had an application method that was resulting in EICP. The protective plastic shield was still used to protect our samples from losing too much solution. Figures 21 through 24 illustrate the Round 2 treatment process.



Figure 21: Native Soil Pan Prior to Spray Application



Figure 22: Application of Dual Solutions



Figure 23: Covered Pans Post Spray Application



Figure 24: Native Soil Pan Turned White from Carbonate

4.3.4 Wind Tunnel Tests and Results

The method used for wind tunnel testing of the Round 2 soil specimens did not change from our Round 1. Wind speed was increased at a steady pace until we saw visual lift off of soil particles. The Round 2 results are presented in the following text.

Mine Tailings

We started out this test at a velocity of 3 m/s. When treated with a control solution of just calcium chloride and urea the detachment velocity was 14.5 m/s with a 0.05 M solution, 14.25 m/s with a 0.1 M solution, and 15 m/s for the 0.2 M solution. When testing the samples that were sprayed with enzyme solution we got results of 16 m/s with a 0.05 M solution, 14 m/s with a 0.1 M solution, and 21 m/s for the 0.2 M solution. The results are shown on Table 14 and Figure 25.

Mine Tailings (Round 2)			
Pan #	Erosion control Method	Avg. DV (m/s)	Avg. DV (mph)
22	0.05 M Control	14.5	32.44
23	0.05 M + Enzyme	15.9	35.79
24	0.05 M + Enzyme	16.0	35.78
25	0.1 M Control	14.3	31.88
26	0.1 M + Enzyme	13.8	31.32
27	0.1 M + Enzyme	13.5	30.20
28	0.2M Control	15.0	33.55
29	0.2 M + Enzyme	21.0	46.98
30	0.2 M + Enzyme	22.0	49.21

Table 14: Mine Tailing Wind Tunnel Results at a rate of 24 l/m² of calcium chloride/urea and 16 l/m² of urease

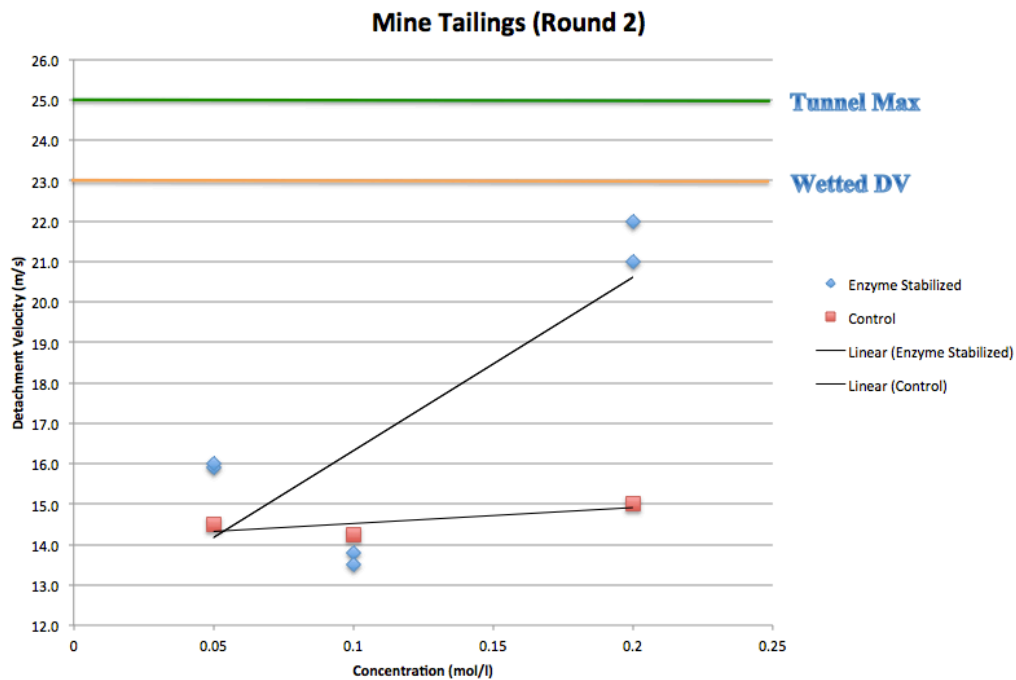


Figure 25: Detachment Velocity for Control and Enzyme Stabilized Mine Tailings Samples at a rate of 24 l/m² of calcium chloride/urea and 16 l/m² of urease

F60 Sand

We started out this test at a velocity of 3 m/s. When treated with a control solution of just calcium chloride and urea the detachment velocity was 13.5 m/s with a 0.05 M solution, 16.7 m/s with a 0.1 M solution, and 18.6 m/s for the 0.2 M solution. When testing the samples that were sprayed with enzyme solution we got results of 19.5 m/s with a 0.05 M solution, 24.75 m/s with a 0.1 M solution, and greater than 25 m/s for the 0.2 M solution. The results are shown on Table 15 and Figure 26.

F60 (Round 2)			
Pan #	Erosion control Method	Avg. DV (m/s)	Avg. DV (mph)
31	0.05 M Control	13.5	30.2
32	0.05 M + Enzyme	18.0	41.38
33	0.05 M + Enzyme	20.5	45.86
34	0.1 M Control	16.7	37.36
35	0.1 M + Enzyme	25.0	55.92
36	0.1 M + Enzyme	24.5	54.8
37	0.2 M Control	18.6	41.61
38	0.2 M + Enzyme	>25.0	>55.92
39	0.2 M + Enzyme	>25.0	>55.92

Table 15: F60 Wind Tunnel Results at a rate of 31 l/m²

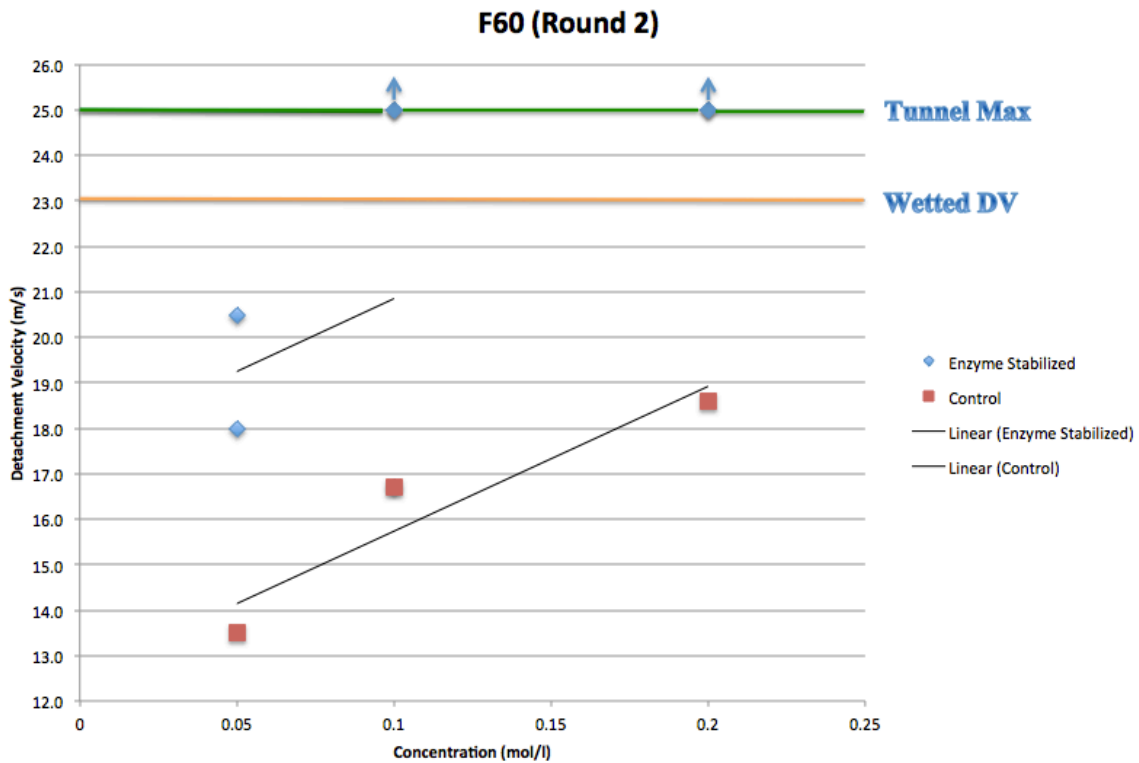


Figure 26: Detachment Velocity for Controls and Enzyme Stabilized Samples F60 samples at a rate of 31 l/m²

Native Soil

We started out this test at a velocity of 3 m/s. When treated with a control solution of just calcium chloride and urea the detachment velocity was 12.5 m/s with a 0.05 M solution, 18 m/s with a 0.1 M solution, and greater than 25 m/s for the 0.2 M solution. When testing the samples that were sprayed with enzyme solution we got results of 13.25 m/s with a 0.05 M solution, and greater than 25 m/s for the 0.1 M and 0.2 M solution. The results are shown on Table 16 and Figure 30.

Native Soil (Round 2)			
Pan #	Erosion control Method	Avg. DV (m/s)	Avg. DV (mph)
40	0.05 M Control	12.5	27.96
41	0.05 M + Enzyme	13.0	29.08
42	0.05 M + Enzyme	13.5	30.2
43	0.1 M Control	18.0	40.26
44	0.1 M + Enzyme	>25.0	>55.92
45	0.1 M + Enzyme	>25.0	>55.92
46	0.2 M Control	>25.0	>55.92
47	0.2 M + Enzyme	>25.0	>55.92
48	0.2 M + Enzyme	>25.0	>55.92

Table 16: Native Soil Wind Tunnel Results at a rate of 31 l/m².

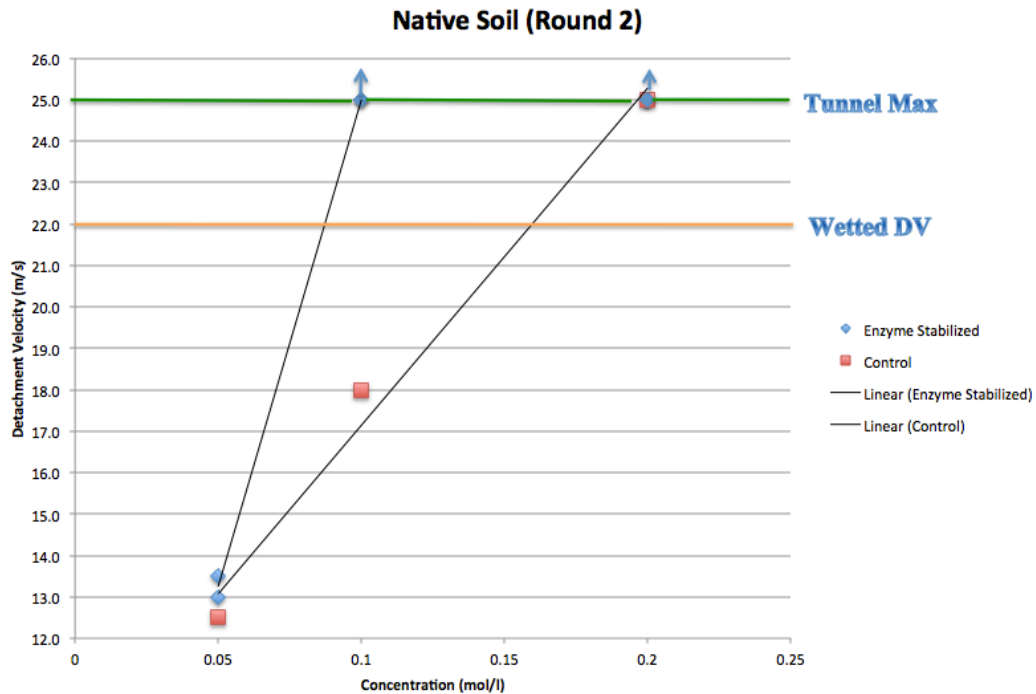


Figure 27: Detachment Velocity for Controls and Enzyme Stabilized Samples Native Soil Samples at a rate of 32 l/m²

4.3.5 Lessons Learned from Round 2 Testing

Following completion of the Round 2 tests, there were still some issues that needed to be addressed. The irregular pattern of some of the results suggested that a repeatability study should be conducted, and further analysis of soil crusts were necessary to see if we were achieving the desired interparticle cementation.

4.4 Repeatability Study

Our objective for the first two rounds of wind tunnel testing was to determine an “optimum” concentration of calcium chloride, urea, and urease enzyme, i.e. a concentration that achieved an erosion resistance similar to that of wetted soil. Our initial plan was to treat 5 soil pans at the optimum concentration to see what the scatter in results would be. However, at the completion of Round 2 testing, we were satisfied with our ability to determine the “optimum” concentration. So in an attempt to increase our confidence in the results we decided to do additional testing at two concentrations. So, in a third round of testing, we tested two sets of three pans at different enzyme stabilized concentrations. This testing also included additional control pans for more results.

4.4.1 Soil Type and Specimen Preparation

For the third round of testing we decided to use the mine tailings. This round of testing consisted of 9 pans. The first three pans consist of two control pans and one pan that was an enzyme stabilized pan at a relatively high concentration. This set of three pans consisted of a 0.4 M control, a 0.5 M control, and a 0.4 M enzyme stabilized pan. The 6 other pans being used for the third round involve lower concentrations, including 3 pans of enzyme stabilized soil at a concentration of .15 M and 3 more enzyme stabilized soil pans at a concentration of .3 M. The preparation method used for these plans is described in the following text.

Pans 49-51 (0.15 M)

- 10 Scoops of soil
- Densified with 5 spoon taps for each quarter turn of the pan

- Lifted and dropped 3 times
- Broke up soil clumps
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Lifted and dropped 3 times
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Evened with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Scraped excess soil of the pan.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
49	1880.00	1.34	83.89
50	1860.00	1.32	82.89
51	1880.00	1.34	83.89

Table 17: Pan Densities for Pans 49-51

Pans 52-54 (0.3 M)

- 15 Scoops of soil
- Densified with 5 spoon taps for each quarter turn of the pan
- Lifted and dropped 3 times
- Broke up soil clumps
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Lifted and dropped 3 times
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Scraped excess soil of the pan.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
52	1840.00	1.31	81.12
53	1880.00	1.34	83.89
54	2030.00	1.45	90.58

Table 18: Pan Densities for Pans 52-54

Pans 55-57

- 15 Scoops of soil
- Densified with 5 spoon taps for each quarter turn of the pan
- Lifted and dropped 3 times
- Broke up soil clumps
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Lifted and dropped 3 times
- Tapped on pan and soil clumps to even soil with a flat edge ruler
- Evened with a flat edge ruler
- Densified with 5 spoon taps for each quarter turn of the pan
- Evened with a flat edge ruler
- Scraped excess soil of the pan.

Pan #	Mass (g)	Density (g/cm³)	Unit Weight (lb/ft³)
55	1790.00	1.28	79.87
56	1800.00	1.29	80.21
57	1810.00	1.29	80.76

Table 19: Pan Densities for Pans 55-57

4.4.2 Urease Solution Preparation

For the Round 3 pans, the same application procedure was used as employed in Round 2. A volume of 200 ml of cementation solution was sprayed on to the surface in four passes of 50 ml. The 200 ml solution included 155 ml of the calcium chloride/urea solution and 45 ml of the urease enzyme solution prepared at the appropriate concentrations and mixed together. The solutions were prepared as follows:

Solution 1: 1300 ml @ 0.5 M CaCl₂ and 0.75 M Urea

$$CaCl_2 = 0.5 \frac{mol}{l} * 147.01 \frac{g}{mol} * 1.3 l = 95.557 \text{ grams of } CaCl_2$$

$$Urea = 0.75 \frac{mol}{l} * 60.06 \frac{g}{mol} * 1.3 l = 58.559 \text{ grams of } Urea$$

200 ml of the solution above will be enough to spray the 0.5 M Control pan. Therefore, 160 ml of this solution was used to create the 0.4 M Control solution.

$$160 \text{ ml @ } 0.5 \text{ M conc.} + 40 \text{ ml of water} = 200 \text{ ml @ } 0.4 \text{ M conc.}$$

To make the 0.3 M solution, we need to adjust our target concentration to account for the extra dilution of the enzyme.

$$0.3 \text{ M } CaCl_2 = \left(\frac{155 \text{ ml}}{200 \text{ ml}} \right) (X) \Rightarrow X = 0.387 \text{ M } CaCl_2$$

Now took 360 ml of the 0.5 M solution to create the 0.387 M calcium chloride (CaCl₂) solution.

$$360 \text{ ml @ } 0.5 \text{ M conc.} + 105.09 \text{ ml of water} = 465 \text{ ml @ } 0.387 \text{ M conc.}$$

The same procedure must be completed for the 0.15 M solution. The concentration needs to be adjusted to account for the extra dilution of the enzyme.

$$0.15 \text{ M CaCl}_2 = \left(\frac{155 \text{ ml}}{200 \text{ ml}}\right)(X) \Rightarrow X = 0.1935 \text{ M CaCl}_2$$

We took 179.955 ml of the 0.5 M solution to create the 0.1935 M calcium chloride solution.

$$179.955 \text{ ml @ } 0.5 \text{ M conc.} + 285.045 \text{ ml of water} = 465 \text{ ml @ } 0.1935 \text{ M conc.}$$

When it was time to make the solution for pan 55, we realized we made a mistake in our initial calculations. When you adjust for enzyme dilution with a 0.4 M solution, we ended up determining a concentration higher than 0.5 M.

$$0.4 \text{ M CaCl}_2 = \left(\frac{155 \text{ ml}}{200 \text{ ml}}\right)(X) \Rightarrow X = 0.516 \text{ M CaCl}_2$$

So now we have to add more constituents to a 0.5 M solution in order to create this solution. We had 365 ml remaining of 0.5 M solution to work with in order to create the desired 465 ml of solution. I used the following calculation.

$$(365 \text{ ml}) \left(0.5 \frac{\text{mol}}{\text{liter}}\right) + (100 \text{ ml})(X) = (465 \text{ ml}) \left(0.516 \frac{\text{mol}}{\text{liter}}\right)$$

$$X = 0.5744 \frac{\text{mol}}{\text{liter}}$$

After creating all five solutions, we needed to adjust the pH of the solutions to create conditions favorable for EICP. We want a solution pH between 7.5 and 9.5. So, the pH of the solutions were adjusted as follows:

- pH of 0.15 M CaCl₂ Solution: 9.30
- pH of 0.3 M CaCl₂ Solution: 8.92
- pH of 0.4 M CaCl₂ Solution: 8.81
- pH of 0.4 M CaCl₂ Control Solution: 8.30
- pH of 0.5 M CaCl₂ Control Solution: 8.10

For the enzyme spray we used a 2 grams/liter concentration of urease for the 200 ml batch. But the initial urease solution was only 45 ml. So the urease solution was made as shown below.

$$(200 \text{ ml of solution}) \left(2 \frac{\text{g}}{\text{l}} \right) = (45 \text{ ml of solution})(X)$$

$$X = 0.88 \frac{\text{g}}{\text{l}}$$

Using a concentration of 0.88 grams/liter, we created 45 ml of enzyme solution. We still kept the same concentration of dry milk stabilizer used previously. So:

$$\text{Urease} = 0.88 \frac{\text{g}}{\text{l}} * 0.45 \text{ l} = 0.3564 \text{ grams of Urease}$$

$$\text{Dry Milk} = 4 \frac{\text{g}}{\text{l}} * 0.45 \text{ l} = 1.62 \text{ grams of Dry Milk}$$

4.4.3 Application Method

Similar to pans 31-48, we would mix up 200 ml of total solution. But we only prepared 3 pans at one time. So, we would spray each pan with 50 ml of soil and then spray one of the three with the remaining 50 ml of solution. We then applied a different pan with the final 50 ml in each round of 200 ml. We then repeated that process 3 times so that all the pans received the full 200 ml of solution. We gave the pans a minute or two in between rounds to allow for some cementation to occur. The control pans received a full 200 ml of solution in four rounds of 50 ml, but there was only about a minute between each round.

4.4.4 Wind Tunnel Tests and Results

The wind tunnel testing procedure remained the same as the previous tests. Spray method one involves applying solutions separate, and spray method 2 involves spraying solutions together. The test results are presented in Tables 20 and 21 and Figures 28, 29, and 30.

Mine Tailings (Round Three)			
Pan #	Erosion control Method	Avg. DV (m/s)	DV (mph)
49	0.15 M + Enzyme	21.5	48.09
50	0.15 M + Enzyme	17.0	38.03
51	0.15 M + Enzyme	24.4	54.58
52	0.3 M + Enzyme	20.5	45.75
53	0.3 M + Enzyme	17.9	40.04
54	0.3 M + Enzyme	21.7	48.54
55	0.4 M Control	11.0	24.61
56	0.5 M Control	15.7	35.12
57	0.4 M + Enzyme	>25	>55.92

Table 20: Round 3 Wind Tunnel Results at a rate of 31 l/m²

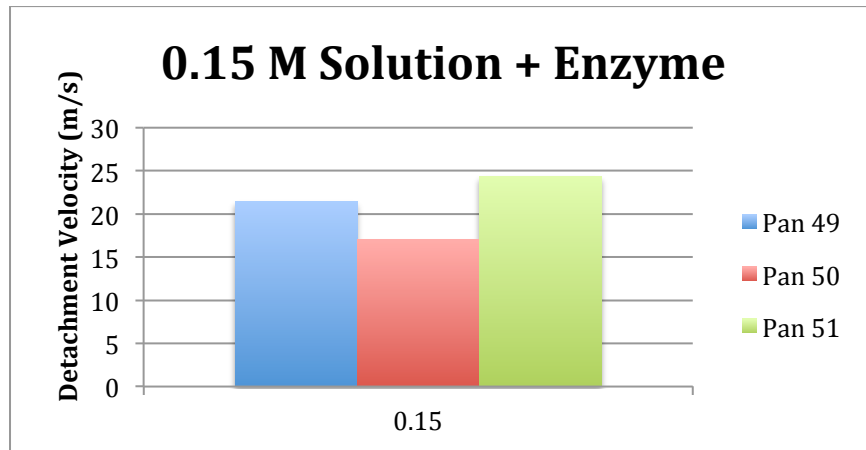


Figure 28: Detachment Velocity for 0.15 M Concentration

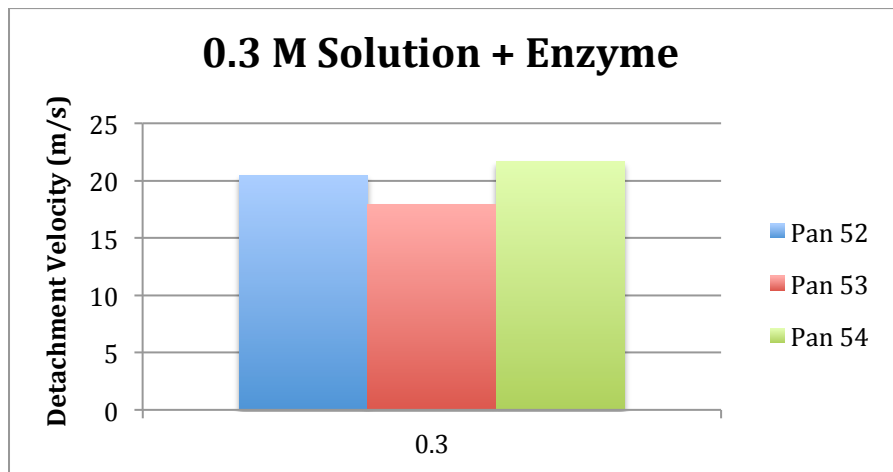


Figure 29: Detachment Velocity for 0.3 M concentration

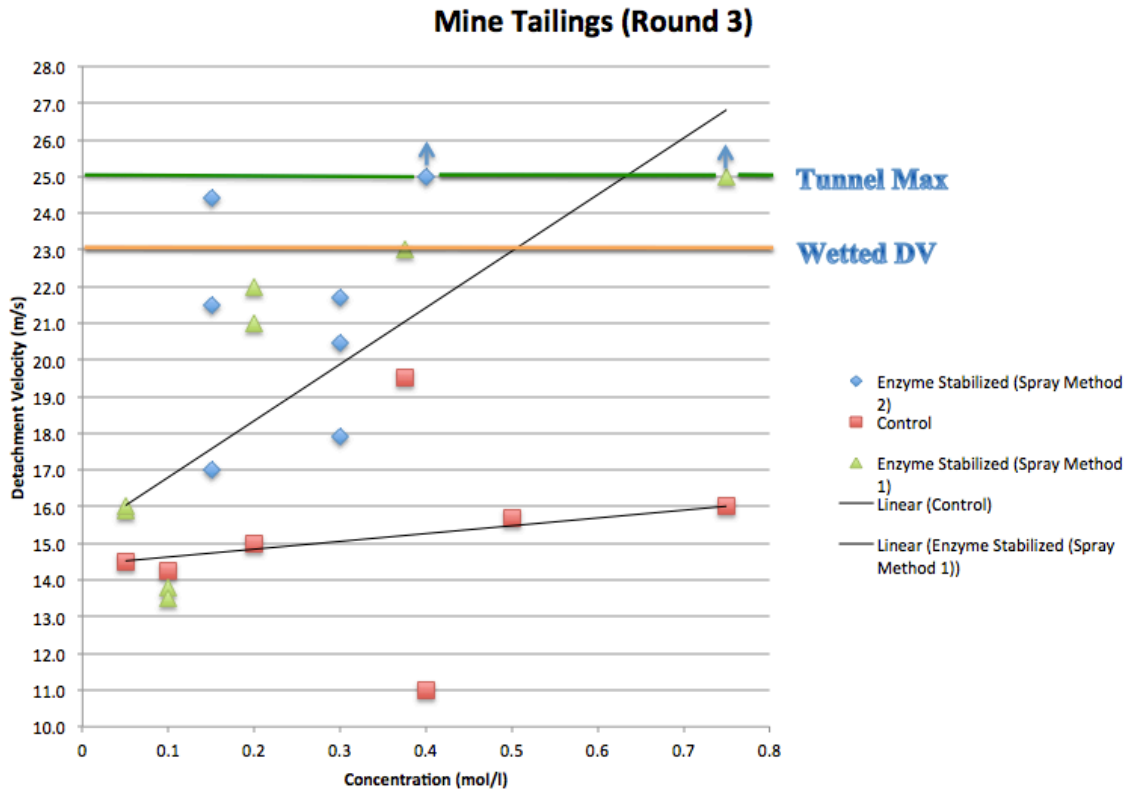


Figure 30: Mine Tailing Detachment Velocity, Rounds 2 and 3 Testing

Initially we thought that the repeatability study would help our results by not only increasing the amount of information in our data plots of detachment velocity vs. concentration, but we thought that we would be able to show good repeatability between each pan. However, our results did not help very much in each area. We believe that the unfavorable results are due to our improved method of application. Since we can make stronger pans with a lower concentration, it gives our soil higher detachment velocities at lower concentrations. From figure 30 we can see the data for both spray methods are shown on the data plot. There is also an obvious issue with our control points around the 0.4 M concentration. I believe one got over sprayed and possible contaminated with enzyme while the other was under sprayed. We also feel that our improvement in application methods caused our solution and enzyme curve to become skewed. More tests will need to be done using the improved spray method in order to improve this curve.

CHAPTER 5

Supplemental Testing

In addition to wind tunnel testing, supplemental testing was conducted to establish the nature of the cemented soil crusts. The goal of this thesis is to achieve enzyme induced carbonate precipitation. However, some of the treated pans did not show visible evidence of carbonate precipitation and we were concerned some of the additional wind resistance of treated specimens came from precipitated salts in soil pores and at interparticle contacts. Thus we wanted to test for carbonate content in the treated soil. In order to test for carbonate, we used a variety of methods. These methods included acid digestion of crust samples and SEM analysis. We also measured crust thickness and conducted a simple water erosion test.

5.1 Crust Sampling and Testing

The first step in our process of determining the presence of carbonate was taking crust samples. Crust samples were taken from most of our treated pie pan testing specimens. However, we did not have crust samples from the Round 1 specimens: we had already thrown out these samples before we started to take crust samples.

5.1.1 Overview of Crust Sampling Technique

The crust sampling technique varied between each soil type. The goal of our crust sampling was to take typically 1in x 1in samples for testing. Sometimes we had pan disturbance during transport back to our lab from the wind tunnel and we just used the broken soil pieces as our crust samples. If we didn't have broken soil pieces, then we needed to extract crust samples. The typical technique used to extract crust samples involved a screwdriver and a metal spatula. We typically used the screwdriver to penetrate the crust in a square pattern. By penetrating the crust all around a specific area it usually broke away from the soil below. If the crust didn't come out easily, then a metal spatula was used to penetrate underneath the crust sample and lift it out. Typically 4 samples were taken from each specimen. We took three crust thickness measurements on the four specimens. We felt that the average of these measurements was a more representative value of crust thickness to report than a single value. Having multiple

specimens also allowed us to use one sample for acid digestion and another for SEM analysis. Figures 31, 32, and 33 show crust samples and crust sampling.



Figure 31: Crust Samples of F60



Figure 32: Crust Samples Being Taken in the Laboratory



Figure 33: Taking Measurements of Crust Samples.

5.1.2 Overview of Samples Taken

Samples of crust from treated specimens of all three soil types were taken. It seemed that the soils with the greater fines fraction had thicker crusts. This may be due to capillary retention of the cementation solution and suction due to capillarity in the soil. The results of crust thickness measurements are shown in Tables 21 - 23.

Native Soil		
Pan Number	CaCl ₂ Concentration (mol/liter)	Avg. Crust Thickness (cm)
3	1 M	0.64
4	1 M + enzyme	0.48
5	2 M + enzyme	0.40
11	2 M + enzyme	0.42
40	0.05 M	1.66
41	0.05 M + enzyme	0.40
42	0.05 M + enzyme	0.23
43	0.1 M	0.53
44	0.1 M + enzyme	0.30
45	0.1 M + enzyme	0.23
46	0.02 M	0.40
47	0.02 M + enzyme	0.47
48	0.02 M + enzyme	0.53

Table 21: Native Soil Crust Thicknesses

F60		
Pan Number	CaCl₂ Concentration (mol/liter)	Avg. Crust Thickness (cm)
10	2 M + enzyme	0.33
12	2 M + enzyme	0.40
31	0.05 M	0.33
32	0.05 M + enzyme	0.47
33	0.05 M + enzyme	0.40
34	0.1 M	0.60
35	0.1 M + enzyme	0.33
36	0.1 M + enzyme	0.36
37	0.02 M	0.83
38	0.02 M + enzyme	0.50
39	0.02 M + enzyme	0.53

Table 22: F60 Crust Thicknesses

Mine Tailings		
Pan Number	CaCl₂ Concentration (mol/liter)	Avg. Crust Thickness (cm)
16	.375 M	0.44
15	.75 M	0.38
18	0.75M + enzyme	0.75
19	.375 M + enzyme	0.37
49	0.15 M + enzyme	0.37
50	0.15 M + enzyme	0.37
51	0.15 M + enzyme	0.33
52	0.3 M + enzyme	0.50
53	0.3 M + enzyme	0.33
54	0.3 M + enzyme	0.40
55	0.4 M + enzyme	0.37
56	0.4 M	0.33
57	0.5 M	0.46

Table 23: Mine Tailing Crust Thicknesses

From the tables above we can see that we did not have much of a correlation between crust thickness and cementation solution concentration. Crust thickness initially appeared to depend completely on soil type and fines content. However, we did notice some changes when we switched our application to method two of using both solutions simultaneously. There were thicker crusts on the F60 and Native soil with application method two. When we calculated the mean and standard deviation for each soil's crust samples, we saw that our mine tailings and F60 acted similar compared to the native soil. This is shown in Table 24 and 25.

Soil Type:	Mine Tailings	F60	Native Soil
Average Crust Thickness	.49 cm	.37 cm	.49 cm
Standard Deviation of Crust Thickness	.179	.049	.109

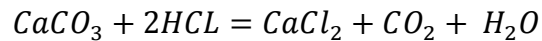
Table 24: Average Crust Sample Thickness and Standard Deviation (Application Method 1)

Soil Type	Mine Tailings	F60	Native Soil
Average Crust Thickness	.38	.48	.53
Standard Deviation of Crust Thickness	.060	.160	.440

Table 25: Average Crust Sample Thickness and Standard Deviation (Application Method 2)

5.1.3 Acid Digestion of Samples

One of the easiest ways to check for carbonate content in a soil is by adding hydrochloric acid to it. When hydrochloric acid is added to a specimen with carbonate present, the carbonate undergoes a reaction that lets off carbon dioxide. This is shown in the following equation.



When the carbon dioxide is released, there are tiny bubbles seen on the surface of the substrate being tested. This can be a quick and easy way to see if there is carbonate available. The exact mass of carbonate can be determined via acid digestion as well by running acid over the soil and by weighing the sample before and after this process. This method for quantifying carbonate content is harder than it sounds. The soil needs to be washed with acid, but the sample loses any soil in this process it will skew the results. For the finer grain soils like mine tailings and native soil, we felt that we would lose too many soil particles for this method to be reliable.

Due to the difficulty in quantifying carbonate content, acid digestion was performed solely check for the presence of carbonate, i.e. we just looked for visible evidence of carbon dioxide bubbles from each sample. Our first sets of crust samples never showed any visible bubbles when exposed to acid. Once we employed the single solution method of spray application, there were better results from acid digestion. Figure 36 shows the acid digestion test being conducted. In Figure 37, we can see that there is intense bubbling occurring when the crust is exposed to acid. This leads us to believe that we have achieved EICP in that soil sample.



Figure 34: Acid Digestion Being Performed

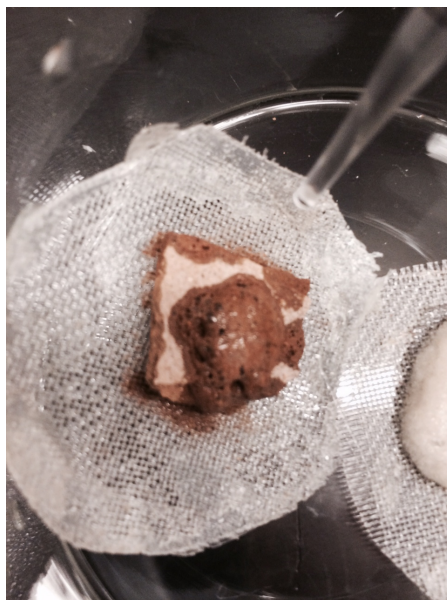


Figure 35: CO₂ Generation due to HCL

5.1.4 SEM Images of Crust Samples

We used a scanning electron microscope (SEM) to take a closer look at the crust samples for evidence of carbonate precipitation. ASU has a SEM in the LeRoy Eyring Center for Solid State Science. This center is an advanced laboratory that holds multiple electron microscopes and x-ray machines. SEM works by focusing an electron probe of

typically 2-50 nm in diameter onto the specimen. A scan generator simultaneously rasters this focused beam across the sample and drives the x- and y-scan coils of an image monitor (Goldstein, 1981). The SEM can detect multiple signals including secondary electrons (SE), backscattered electrons (BSE), X-rays (EDS), electron-beam-induced current (EBIC), and cathodoluminescence (CL) (Goldstein, 1981). These signals can then be used to create a two-dimensional map of the near-surface topography, composition and possibly electronic nature of the specimen. Spatial resolution is limited both by the size of the focused probe and also by the penetration depth of the specimen excitation (Goldstein, 1981).

Our initial (Round 1) specimens showed no signs of carbonate in the SEM images. This doesn't necessarily mean that it is not there. Our samples had a definite strength increase over the control samples, which we feel is quite possibly due to small amounts of carbonate precipitation. It is possible that the salt evaporite in the Round 1 specimens covered up the carbonate in the SEM images. However, the specimens from the single solution application method clearly showed carbonate crystals in the SEM images.



Figure 36: SEM Image of F60 particle with carbonate precipitation

From the figure above we see a whole F60 particle in the middle of the picture. The substance on the upper right corner of the center particle is believed to be evaporite cementation. However, the chunky cube-like pieces are carbonate precipitation.

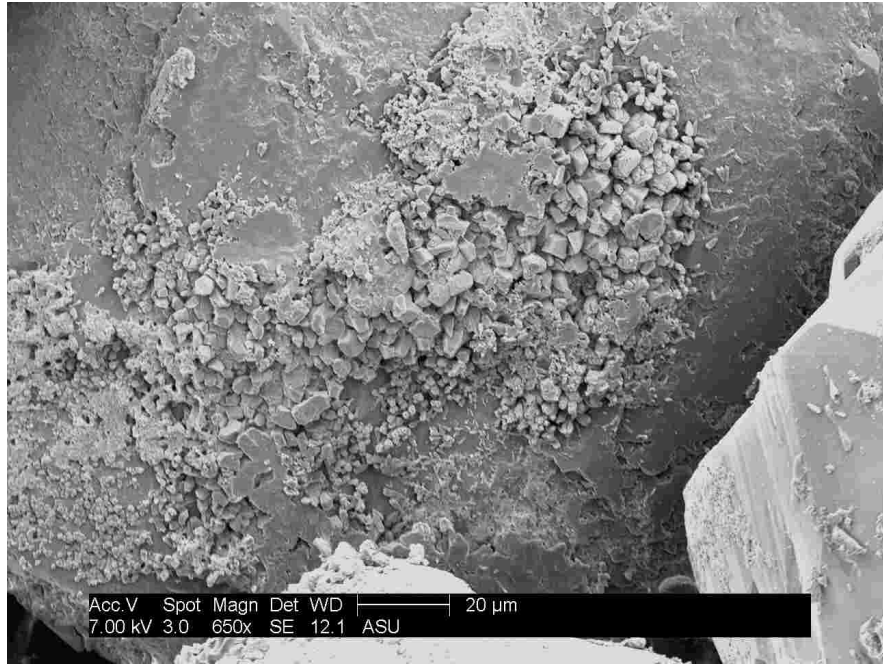


Figure 37: Enlarged version of SEM image in Figure 38.

The figure above is an enlarged version of the previous SEM image. The image gives a better look at the carbonate precipitation on the surface of the F60 particle. We can also see flat faces within the carbonate precipitation that look like a smooth plane. We believe that these are sections where the F60 particle was cemented to other particles via that carbonate precipitation.

5.2 Water Erosion Experimentation

Another test we performed on our treated soil was a water erosion test. In some circumstances, water erosion resistance can be as important as wind erosion resistance. Furthermore, this test potentially could show if some of the cementation in the soil was due to calcium chloride evaporite. Calcium chloride is very soluble in water and will start to break down when it comes into contact with moisture. While continued resistance to erosion when exposed to water does not necessarily mean that carbonate is present, for the treated specimens in this testing program it seemed to be the only reasonable

explanation. So the plan for testing involved exposing treated and control samples to surface water flow for a certain amount of time, watching for visible erosion, and then determining the amount of soil lost for each pan.

5.2.1 Procedure of Testing

For the water erosion test we employed a Nasco Soil Erosion simulator kit. This kit is basically a demonstration kit for science class. The kit uses rectangular soil pans that can be placed on a stand at different slope angles. A water nozzle is provided that can be connected to either a hose or a 1-liter bottle to subject the elevated soil pan to a controlled amount of surface water flow. Two pans of mine tailings were prepared and sprayed with 0.4 M concentration solutions. One specimen was sprayed with calcium chloride and urea only to serve as a control. The second specimen had enzyme in the sprayed-on solution. The water was applied for 3 minutes with the specimens at an angle of 15 degrees from the horizontal.

5.2.2 Apparatus Setup

The spray nozzle was connected to a hose in the laboratory. Before testing our two soil pans, we tested the apparatus on some treated pie pans we had prepared previously. Figure 40 shows the practice set up. Figure 41 shows the control specimen prior to testing.



Figure 38: Practice Set-up for Water Erosion Test



Figure 39: Control Specimen Prior to Testing

5.2.4 Results

The test using the control specimen was run first. The specimen as subjected to surface water flow for 3 minutes. The control specimen held up to erosion well for the first minute of water flow, but it started to absorb a large volume of water relative to what was draining off the specimen. After the specimen seemed to become saturated, large amounts of soil started breaking away from the surface of the pan. The soil that broke away and the water than ran off the specimen was caught in a bucket below the pan. Figure 42 shows the control pan towards the end of the 3 minute application period, after soil started breaking away from the specimen.



Figure 40: Control Pan Mid Test

When the enzyme stabilized soil pan was tested, there was no visual absorption of surface water by the soil. From the image in Figure 43 you can see that the water coalesced in four discrete steams when flowing down the pan. Figure 44 compares the enzyme-stabilized and control samples at the end of the test.

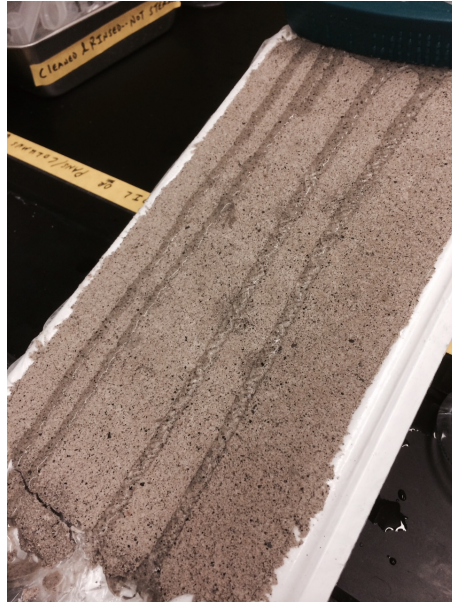


Figure 41: Water Flowing Over the Surface of the Enzyme-Treated Specimen



Figure 42: Water Erosion test Specimens Compared after 3 Minutes of Water Flow

Figure 45 shows the volume of water and soil collected from each specimen during the test. Comparison of the volumes of water collected by the end of the test showed that the control pan absorbed a much larger volume of water than the enzyme stabilized pan.

Furthermore, at the end of the test the surface of the control pan was soft, wet, and plastic while the surface of the enzyme stabilized pan was still hard, with an intact crust.

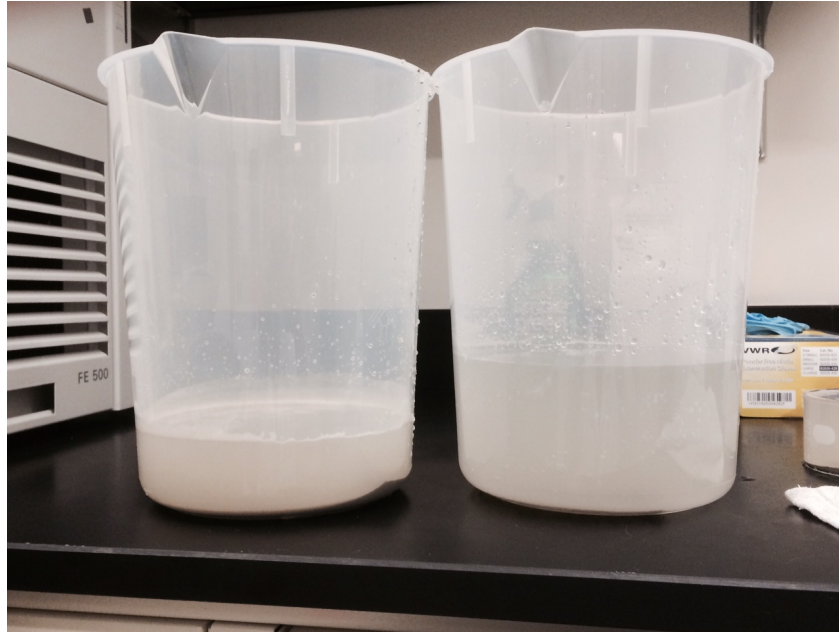


Figure 43: Soil and Water Collected During the Water Erosion Test (Control test bucket of the left).

As shown by Figure 45, less water flowed off of the control pan during the test, but there was much more soil in the bucket that collected runoff from the control specimen. The bucket collecting runoff from the stabilized specimen had minimal amounts of soil but more than double the amount of water than collected from the control specimen. After allowing some time for the soil particles to settle in the buckets, the water in the buckets was removed and the mass of eroded soil was weighed. The bucket for the control specimen had more than 7 times the soil mass than the bucket for the enzyme treated specimen.

CHAPTER 6

Conclusions & Recommendations

6.1 Summary

Nearly 60 soil specimens were testing in a wind tunnel to evaluate the effectiveness of EICP for mitigation of fugitive dust. Three different soils were tested at cementation solution concentrations varying from .05 M to 2 M in an attempt to create curves relating the detachment velocity to cementation solution concentration. The method of application of the cementation solution varied over the course of the testing program. We eventually determined an efficient spray technique for applying our EICP cementation solution. Supplemental testing, including exposure to acid and scanning electron microscope imaging, was also conducted to establish that the spray technique was actually precipitating carbonate on the test specimens. Finally, we also conducted a simple water erosion experiment to distinguish between carbonate cementation and salt evaporate cementation. The results indicate that EICP has the great potential for control of erosion due to both wind and surface water runoff.

6.2 Conclusions

Our wind tunnel tests show that EICP can be a very effective means of mitigating fugitive dust if applied at proper concentrations. However, more testing needs to be done to perfect the process. In particular, a method of applying the cementation solution in the field needs to be worked out. Ideally, the cementation solution would be applied using a single canister containing the urease solution that is hooked to a water truck containing the calcium chloride and urease solution and the two solutions are mixed together at the nozzle during application.

Overall, this research has provided significant evidence that carbonate precipitation is a viable alternative for dust control. It provides significant strength and has a relatively high resistance to water erosion. Hopefully the findings in this study will facilitate further development of this technology.

6.3 Recommendations for Future Work

We have several recommendations future work. The first thing that needs to be done is to perform additional wind tunnel tests at relatively low concentrations. e.g. concentrations such as .01, .02, .03, and .04, to determine with good confidence the concentration that yields erosion resistance comparable to water. This testing can also shed light on the true shape of the detachment vs. concentration plots.

Another step would be to test the effectiveness of hydrogels or biopolymers as a method of enhancing EICP on the soil surface. The hydrogels or biopolymers like xanthan and guar could retain the enzyme and calcium chloride solution together, providing a more efficient method for carbonate precipitation. There may also be benefit to adding natural fibers to our enzyme solutions in order to increase the tensile strength of the cemented soil.

There also needs to be research on the effects of ammonia and ammonium by-products from the EICP process. While much of the ammonia volatilizes, smell alone may be a problem that will keep urea hydrolysis from being an effective method for dust control in urban areas. The residual ammonium can become a serious problem if it somehow makes its way to the groundwater table. However, there can also be benefits of the ammonium in terms of stimulation of vegetation. Farmers across the world use anhydrous ammonia as a fertilizer and nitrogen source in the soil.

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APPENDIX A

OTTAWA F60 SAND PRODUCT SHEET

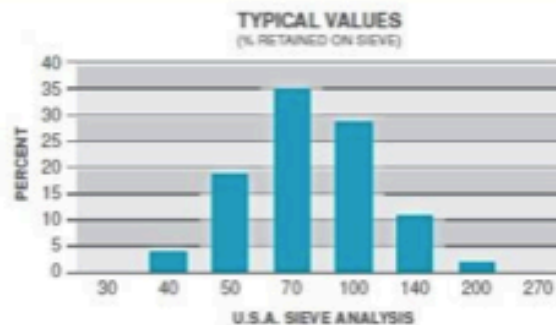
Product Data



F-60

UNGROUND SILICA

PLANT: OTTAWA, ILLINOIS



USA STD SIEVE SIZE		TYPICAL VALUES		
MESH	MILLIMETERS	% RETAINED		% PASSING
		INDIVIDUAL	CUMULATIVE	CUMULATIVE
30	0.600	0.0	0.0	100.0
40	0.425	4.0	4.0	96.0
50	0.300	19.0	23.0	77.0
70	0.212	35.0	58.0	42.0
100	0.150	29.0	87.0	13.0
140	0.106	11.0	98.0	2.0
200	0.075	2.0	100.0	0.0
270	0.053	0.0		

TYPICAL PHYSICAL PROPERTIES

AFS TM Acid Demand (@pH 7)	<1.0
AFS TM Grain Fineness	60
Color	White
Grain Shape	Round
Hardness (Mohs)	7
Melting Point (Degrees F)	3100
Mineral	Quartz
Moisture Content (%)	<0.05
pH	7
Specific Gravity	2.65

TYPICAL CHEMICAL ANALYSIS, %

SiO ₂ (Silicon Dioxide)	99.8
Fe ₂ O ₃ (Iron Oxide)	0.020
Al ₂ O ₃ (Aluminum Oxide)	0.06
TiO ₂ (Titanium Dioxide)	0.01
CaO (Calcium Oxide)	<0.01
MgO (Magnesium Oxide)	<0.01
Na ₂ O (Sodium Oxide)	<0.01
K ₂ O (Potassium Oxide)	<0.01
LOI (Loss On Ignition)	0.1

December 15, 1997

(1) American Foundrymen's Society

U.S. Silica Company
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Frederick, MD 21701
(301) 682-0600 (phone)
(800) 243-7500 (toll-free)
ussilica.com

DISCLAIMER: The information set forth in this Product Data Sheet represents typical properties of the product described; the information and the typical values are not specifications. U.S. Silica Company makes no representation or warranty concerning the Products, expressed or implied, by this Product Data Sheet.

WARNING: The product contains crystalline silica – quartz, which can cause silicosis (an occupational lung disease) and lung cancer. For detailed information on the potential health effect of crystalline silica - quartz, see the U.S. Silica Company Material Safety Data Sheet.

