

SOUTHERN PLAINS
TRANSPORTATION CENTER

**VALIDATING FIELD EMPLOYED X-RAY FLUORESCENCE (XRF) ON
STABILIZED SUBGRADE PROJECTS TO ASSESS IMPACT OF EXTREME
PRECIPITATION EVENTS, IMPROVE CONSTRUCTION QUALITY
CONTROL AND FACILITATE GEOTECHNICAL FORENSIC
INVESTIGATIONS**

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SPTC14.2-02-F

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16. ABSTRACT The goal of this research project was to assist the state in improving stabilized subgrade behavior by providing a fast, easy-to-implement method of testing stabilizer content and distribution during construction, prior to pavement laying. In addition, this method provides a tool for forensic investigations, where the presence or lack of additive in a stabilized layer is in question. The objectives of the proposed research, which support the goal were to validate the portable field employed XRF (PHXRF) test on several roadway stabilization projects to assess the depth and spatial heterogeneity of the stabilization across a site as well as the impact of extreme precipitation events on stabilized subgrade strength. This information can be used to make recommendations to transportation officials on how to employ PHXRF and implement a laboratory XRF testing protocol on job-sites for quality control applications or during forensic investigations. There is a need for this tool as currently there are no simple and accurate methods for making discrete measurements of field additive contents. Results of this research indicate the PHXRF, using the proper sampling and testing protocols, can provide an excellent assessment of the spatial distribution of a soil additive. However, the results also highlight the importance of acquiring adequate samples of the virgin soil, chemical additive, and mixed soil, to properly characterize the additive content distribution in the subgrade.			
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
AREA				
in ²	square inches	645.2	square millimeters	mm ²
ft ²	square feet	0.093	square meters	m ²
yd ²	square yard	0.836	square meters	m ²
ac	acres	0.405	hectares	ha
mi ²	square miles	2.59	square kilometers	km ²
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft ³	cubic feet	0.028	cubic meters	m ³
yd ³	cubic yards	0.765	cubic meters	m ³
NOTE: volumes greater than 1000 L shall be shown in m ³				
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
TEMPERATURE (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
ILLUMINATION				
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.45	newtons	N
lbf/in ²	poundforce per square inch	6.89	kilopascals	kPa
APPROXIMATE CONVERSIONS FROM SI UNITS				
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
AREA				
mm ²	square millimeters	0.0016	square inches	in ²
m ²	square meters	10.764	square feet	ft ²
m ²	square meters	1.195	square yards	yd ²
ha	hectares	2.47	acres	ac
km ²	square kilometers	0.386	square miles	mi ²
VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m ³	cubic meters	35.314	cubic feet	ft ³
m ³	cubic meters	1.307	cubic yards	yd ³
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
TEMPERATURE (exact degrees)				
°C	Celsius	1.8C+32	Fahrenheit	°F
ILLUMINATION				
lx	lux	0.0929	foot-candles	fc
cd/m ²	candela/m ²	0.2919	foot-Lamberts	fl
FORCE and PRESSURE or STRESS				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in ²

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)

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FINAL REPORT

May 15, 2017

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Executive Summary

A large portion of transportation corridor construction projects use lime and other calcium-based stabilizers to reduce soil plasticity, increase soil shear strength, reduce soil compressibility, and reduce soil's tendency to undergo volume change when subjected to variations in water content. In simple terms, additives like lime render highly plastic expansive soils non-plastic and non-expansive. Determining how much stabilizer to add to a specific soil to achieve appropriate and long-term soil parameter changes is no easy feat, but guidelines, such as OHD L-50 and 51 and ASTM D 4609 exist to provide recommendations based on soil classification and type of stabilizer. These recommendations are based on laboratory tests and are performed under certain moisture conditions. There have always been questions about how a laboratory predicted parameter fairs in the field, and in a recent study performed with the ODOT, the PIs found that extreme precipitation events significantly impacted the competency of newly stabilized subgrades. In fact, on several roadway projects tested in 2007, there were extreme precipitation events after the soil subgrade was stabilized, but before the pavement was laid. The subgrade was tested at 0, 1, 7, 14, and 28 days (or until the pavement was laid) and when precipitation occurred during that testing window, the strength significantly decreased in some cases and did not achieve the originally anticipated strength as predicted in the laboratory.

In addition to extreme precipitation events impacting subgrade strength prior to pavement laying, the actual amount and distribution of stabilizer that ends up in the subgrade soil can significantly impact the long-term behavior of the roadway. The amount of stabilizer to be used is specified in the design phase, but currently, there is no reliable way to check how close the field stabilization amount is to the laboratory design amount specified, nor how well the stabilizer is distributed, both spatially and throughout the required design depth. Through previous research, the PIs have found that using X-ray fluorescence (XRF) can accurately detect the amount of stabilizer in a subgrade at any given point, which can help inspection officials make timely corrections if necessary and provide a tool for forensic investigations if a roadway is not behaving as expected. In terms of cases where the stabilized subgrade loses strength due to extreme precipitation events (possibly due to leaching of the stabilizer), the XRF can be used to determine how much additional stabilizer is necessary to bring the roadway back up to design standards. This XRF technique of measuring and monitoring the Calcium content of a stabilized sub-base has the potential to revolutionize construction inspection practice, as well as geotechnical forensic investigations. This research is an important step to implementing XRF in construction protocol and demonstrates how XRF technology can help transportation officials achieve a more uniform and better behaving pavement system.

The purpose of this research was to validate PHXRF on stabilized subgrade projects for construction quality control and geotechnical forensic investigations. This was achieved through two comprehensive rounds of experiments: laboratory testing and field testing. Laboratory testing sought to assess the effects of scan duration, scan technique, sample particle size, and sample type on the precision and accuracy of the SC measurements of the PHXRF devices. Field testing sought to assess how the sampling and testing protocol (e.g., in situ (no soil preparation) and ex situ (some sample preparation)) effected the accuracy of the SC measurements as well as assess relative spatial and depth SC homogeneity of the tested sites. The key findings of this research are as follows. 1) Longer scan durations neither improve nor hinder PHXRF precision and accuracy and are therefore considered negligible. 2) Significant benefits in terms of PHXRF accuracy are observed when particle sizes are reduced from passing No. 4 to passing No. 40, yet the benefits are less significant when particle sizes are reduced further. 3) The relationships between sample type (pressed pellet versus powder) and the precision and accuracy of the PHXRF devices are inconclusive due to conflicting results between OHC and SGB samples. 4) Either a standard scanning technique, where a sample is scanned at the same location three times, or a quartering scanning technique, where a sample is rotated 90° after each scan, may be appropriate for PHXRF SC measurements. 5) When used in the field, the PHXRF device performs poorly in situ (e.g., no sample preparation) during direct measurement on the surface of the treated subgrade. 6) However, when samples are removed and tested, the PHXRF device performs well ex situ (e.g., sampling and processing soil over a #40 sieve). 7) The linear relationship between ex situ measurements and commercial XRF SC measurements has an r^2 value of 0.925, which suggests that PHXRF measurements can be mathematically corrected to obtain a truer SC value. 8) PHXRF is a convenient way of gathering data needed to assess the spatial and depth heterogeneity of stabilized subgrade sites.

Introduction

A large portion of transportation corridor construction projects use lime and other calcium-based stabilizers to reduce soil plasticity, increase soil shear strength, reduce soil compressibility, and reduce soil's tendency to undergo volume change when subjected to variations in water content. In simple terms, additives like lime render highly plastic expansive soils non-plastic and non-expansive. Determining how much stabilizer to add to a specific soil to achieve appropriate and long-term soil parameter changes is no easy feat, but guidelines, such as OHD L-50 and 51 and ASTM D 4609 exist to provide recommendations based on soil classification and type of stabilizer. These recommendations are based on laboratory tests and are performed under certain moisture conditions. There have always been questions about how a laboratory predicted parameter fairs in the field, and in a recent study performed with the ODOT, the PIs found that extreme precipitation events significantly impacted the competency of newly stabilized subgrades. In fact, on several roadway projects tested in 2007, there were extreme precipitation events after the soil subgrade was stabilized, but before the pavement was laid. The subgrade was tested at 0, 1, 7, 14, and 28 days (or until the pavement was laid) and when precipitation occurred during that testing window, in some cases the strength determined in situ decreased significantly (Snethen et al. 2008).

In addition to extreme precipitation events impacting subgrade strength prior to pavement laying, the actual amount and distribution of stabilizer that ends up in the subgrade soil can significantly impact the long-term behavior of the roadway. The amount of stabilizer to be used is specified in the design phase, but currently, there is no reliable way to check how close the field stabilization amount is to the laboratory design amount specified, nor how well the stabilizer is distributed, both spatially and throughout the required design depth. Through previous research (Cerato and Miller 2013), the PIs have found that using X-ray fluorescence (XRF) with a proper testing protocol, the amount of stabilizer in a subgrade at any given point can be accurately determined, which can help inspection officials make timely corrections if necessary and provide a tool for forensic investigations if a roadway is not behaving as expected. In terms of cases where the stabilized subgrade loses strength due to extreme precipitation events (possibly due to leaching of the stabilizer), the XRF can be used to determine how much additional stabilizer is necessary to bring the roadway back up to design standards. This XRF technique of measuring and monitoring the Calcium content of a stabilized sub-base has the potential to revolutionize construction inspection practice, as well as geotechnical forensic investigations. This research project details the validation of the portable, handheld XRF (PHXRF) on several stabilized subgrade sites throughout the state. The results clearly show the importance of implementing XRF in construction protocol and how it can help construction officials achieve a more uniform and better behaving pavement system.

Objectives and Scope of Research

The goal of this research project was to assist the state in improving stabilized subgrade behavior by providing a fast, easy-to-implement method of testing stabilizer content and distribution during construction, prior to pavement laying. In addition, this method provides a tool for forensic investigations, where the presence or lack of additive in a stabilized layer is in question. The objectives of the proposed research, which support the goal were to validate the portable field employed XRF (PHXRF) test on several roadway stabilization projects to assess its accuracy in detection. In addition, the PHXRF was used to assess the depth and spatial heterogeneity of the stabilization across a site as well as the impact of extreme precipitation events on stabilized subgrade strength. This information can be used to make recommendations to transportation officials on how to employ PHXRF and implement a laboratory XRF testing protocol on job-sites for quality control applications. In addition, XRF can be utilized after extreme precipitation events to assess losses of stabilizer possibly due to leaching, or during forensic investigations, where the presence or lack of additive in a stabilized layer is in question.

Impacts of Research

Currently there are no simple and accurate methods for making discrete measurements of field additive contents. The XRF technique could be an extremely useful tool to use for quality control applications or during forensic investigations, where the presence or lack of additive in a stabilized layer is in question. ODOT will be able to incorporate the PHXRF testing protocol into their construction quality control program.

Research presented herein demonstrates that with proper testing protocols, PHXRF can be used to detect subgrade stabilization adequacy, which is hugely important. However, the positive impacts of this initial study will continue as new ideas spawned from this work are pursued. The knowledge gained through the current research can be leveraged to pursue other fruitful research endeavors. For example, a natural extension of this work is to conduct research to demonstrate and validate the use of PHXRF for sulfate testing in soil subgrades and environmental applications, and so PHXRF has a wide spectrum of possible applications for ODOT. Preliminary work associated with agricultural science has shown that the PHXRF can be used to detect sulfate (SO_4) in soils (Weindorf et al. 2008 & 2009), and so lessons learned from the current study can be applied to develop testing protocols for subgrade stabilization work. Therefore, the PHXRF can serve several purposes on site, since sulfate detection changes any stabilization protocol because of the threat of ettringite formation.

SPTC Vision and Mission

Developing an efficient, portable, accurate method for measuring subgrade stabilization immediately after mixing and before laying pavement is directly in line with the SPTC mission to develop comprehensive, cost-effective, and imminently implementable solutions to critical infrastructure-related issues facing the transportation systems of the

region and the nation. In addition, the research outcomes of this project align with the SPTC vision, which is to be a diverse and inclusive regionally-based, nationally-recognized research, education and outreach center dedicated to solving pressing transportation and freight infrastructure problems and producing highly trained transportation professionals.

Background

The ability of x-ray fluorescence (XRF) analysis to measure trace elements in multiple applications is extensive in the literature; however, until recently, no information was available showing its applicability to measuring chemical additive content in stabilized soil subgrades (Cerato and Miller 2013). Current methods for estimating stabilizer content of soils are fairly cumbersome (e.g., ASTM D3155 Standard Test Method for Lime Content of Uncured Soil–Lime Mixtures), limited in scope, and not very accurate. Other methods used in soil stabilization design that have been presented in the literature [e.g., the lime fixation capacity method (Hilt and Davidson 1960; Eades and Grim 1966), initial consumption of lime (ICL) test (Rogers and Glendinning 1996), and unconfined compressive strength test (ASTM D4609)], can be thought of as indicator tests. These are used to determine how much stabilizer to add, for example, to reach a *pH* of 12.4, indicating a saturated solution of lime, or gain sufficient strength, respectively; they cannot be retroactively used to pinpoint how much stabilizer is actually present in the soil. It seems logical, therefore, that an easier, more accurate method to determine stabilizer content would be of great benefit to transportation officials.

The XRF method has been used in environmental applications to measure changes in chemical composition in soils for pollution monitoring (Baranowski et al. 2002) and chemical weathering rates (elemental losses) in sand dunes (Esser et al. 1992) and clayey soil (Starr and Lindroos 2006). It has also been used to detect trace elements in drinking and surface waters (Zawisza and Sitko 2006) and to identify airborne elements in aerosol samples collected in industrial areas (Abdelbagi et al. 2011). XRF techniques are also used in agronomic analyses including measurement of macronutrients for land management in agricultural crops (Morgenstern et al. 2010), detection of gypsum in soils (Weindorf et al. 2008), and identification and verification of archaeological artifacts through detection of trace-element composition (Constantinescu et al. 2010). Chakrabarti and Kodikara (2007) used XRF analyses to determine trace elements in basaltic rock and cementitious binders when studying the microstructure of cementitiously stabilized pavement materials to relate the microstructural development of the binders to the development of mechanical properties.

From the successes in the laboratory using XRF, several portable field XRF (PXRF) devices were developed. These PXRF devices have been used in environmental applications, such as measuring heavy metals and toxic elements in water and soil sources (Swift 1995; Shesky 1997; Elam et al. 1997a & b; Chou et al. 2010), and anthropological applications, which include the determination of elemental concentration in fine-grained metamorphic and sedimentary rock

gravestones from early medieval Ireland (Gunter et al. 2010). PHXRF results were compared with more extensive laboratory methods, such as atomic absorption spectrometry (AAS) or inductive coupled plasma–atomic emission spectrometry (ICP-AES) and showed good correlation (Melquiades and Appoloni 2004).

Past and Current Effort

Over the past six years, both the PI and co-PI, and their students, have been working on developing the XRF method to determine soil stabilizer content in roadway sub-bases. Their paper, Cerato and Miller (2013), details this technique through an extensive validation study and implementation program for four Oklahoma Department of Transportation (ODOT) road-widening project sites stabilized with either quicklime or Calcium Fly Ash (CFA).

Validation of Control Samples

A suite of validation control samples were sent along with the field test samples to a commercial laboratory to assess the accuracy of using XRF to determine stabilizer content using the “Whole Rock Analysis” technique. Samples of the untreated soil, as well as the chemically stabilized soil from each field test site were prepared by processing over a U.S. #80 sieve, as specified by the commercial laboratory, and approximately 50 g of soil was sent for testing. It should be noted that processing for this application requires all of the sample to pass the #80 sieve, by grinding if necessary, as opposed to typical soil processing methods where larger particles are removed. Thirteen different elemental contents were determined, as well as loss on ignition (LOI). The resulting percentages (by dry weight) were provided by the commercial laboratory, and CaO was used as the elemental compound to calculate the percentage of chemical additive in the field samples. This was done simply by taking the difference (increase) in CaO (% of dry weight) between the treated and untreated soil and dividing by the difference of CaO in the additive and untreated soil.

$$SC = \left[\frac{CaO_f - CaO_0}{CaO_{CA} - CaO_0} \right] \times 100\% \quad [1]$$

where:

SC is the chemical stabilizer content in the chemically stabilized soil sample (% of dry weight),

CaO_f is the amount of CaO measured by XRF in the chemically stabilized soil sample (%),

CaO₀ is the amount of CaO measured by XRF in the untreated natural soil sample (%), and

CaO_{CA} is the amount of CaO measured by XRF in the chemical additive (%).

The average results and standard deviation for four validation soils with all additive amounts were plotted together (Figure 1). The XRF technique accurately measured the amount of three different stabilizers in each soil tested. The standard deviation and coefficients of variation (COVs) within each triplicate soil set ranged from 0–0.70 and 0–0.13, respectively. In addition, the deviation between sample sets was relatively small. The accuracy to which the XRF technique is able to measure the actual amount of stabilizer amount in four different soils tested with three different stabilizers is a positive indicator that this technique can be applied to field sites.

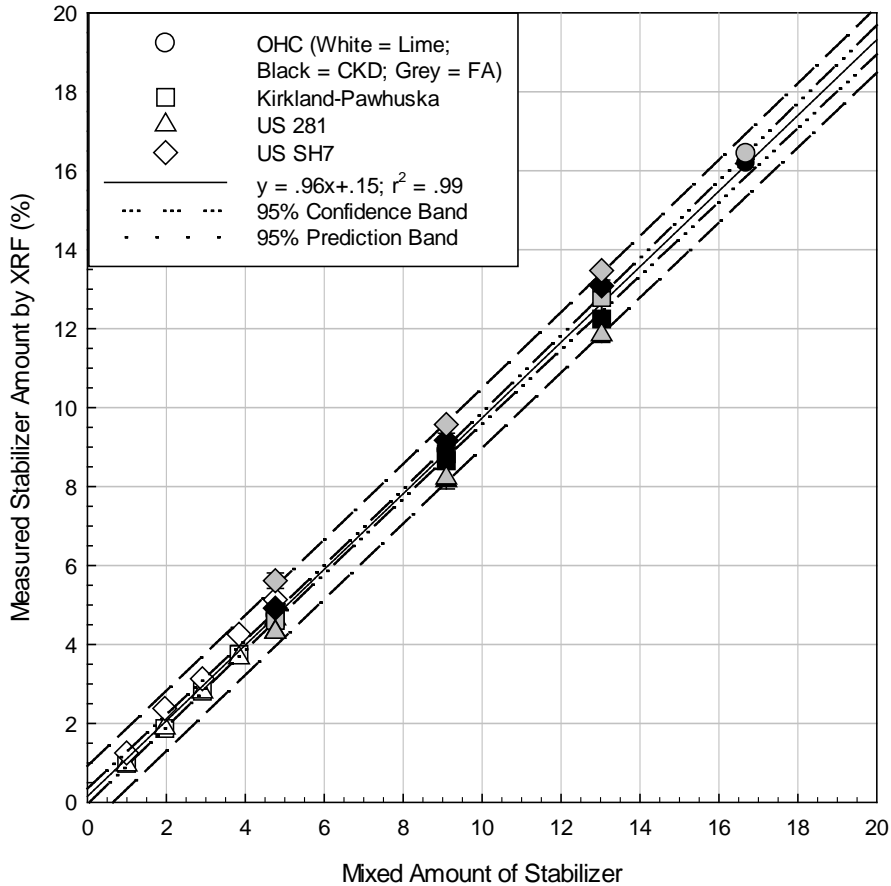


Figure 1: Average Measured Stabilizer Amount in Soils stabilized with Lime, CKD and Fly Ash.

Implementation at Field Sites

The validated XRF method was employed on several ODOT chemical stabilization roadway projects to determine exactly how much stabilizer had been placed in the roadbed compared to what the design specifications called for. The specified design contents were provided by the contractors. The sites were sampled and the soil sent to a commercial laboratory for testing. For Sites #1 and #2, the XRF determined content was higher than the design specified

content, but for Sites #3 and #5, the XRF measured stabilizer amount was lower than what was specified (Table 1).

Table 1: XRF Determined Additive Content Comparison.

Site Number	Soil Name	Type of Stabilizer	Design Specified Content (%)	XRF Determined Content (%)
#1	US 281	CFA	14	15.38
#2	Penn Ave.	CFA	12	13.39
#3	US 177	Quicklime	2.72	2.34
#4	SH 7	Quicklime & CFA	4 , 12	N/A
#5	US 81	CFA	14	12.15

RESULTS

PHXRF Laboratory Testing

From the success of the XRF Laboratory Validation studies, it was hypothesized that the portable handheld XRF (PHXRF) technique could be utilized with good results as well. The appeal of the PHXRF method is how quickly and easily a result can be returned; however, there has not been a lot of quantitative work on soils using the PHXRF. Some previous research shows how grain-size can affect the XRF signals (e.g., Maruyama 2008, Imanishi et al. 2010, Markowicz 2011). This is avoided in the laboratory setting by melting the soil into a glass disc, which becomes infeasible in the field. Another method, called the pressed pellet, is made by crushing the soil past a certain sieve, mixing with a binder, and squeezing with 12-25 tons of force into a “pressed pellet” for testing. Yet another method would be to simply process the soil to a uniform grain size and test the powder in a cup. What would happen, however, if the PHXRF were used directly on the stabilized layer, with no sample preparation at all? Would the results be as good as the proven laboratory methods? In order to find out how accurately the PHXRF unit could possibly read in the field, a laboratory study was first conducted on several testing variables including scan duration, scan technique, particle size and sample type, to determine the effect on the precision and accuracy of the results. Once these effects were quantified, the PHXRF was utilized on five field sites. The two PHXRF units that were used in this study were the Bruker S1 Titan (Device A) and the Thermo Scientific XL3t-950 GOLDD+ (Device B). The first was rented from the manufacturer, and the second was rented from a colleague in the Civil Engineering Department at OU.

Description of Analysis

The Stabilizer Content (SC) results of the two PHXRF devices were compared to "Whole Rock Geochemistry" results received from laboratory XRF in order to determine

the sample preparation and analysis techniques that produce the most accurate and repeatable results. First, a one-way analysis of variance (ANOVA) was conducted to prove statistical significance between the PHXRF SC measurements of different sample preparation and analysis techniques. If it was found that a statistically significant difference exists between preparation and analysis techniques, then an accuracy analysis comprising regression equations, coefficients of determination (r^2), 95% confidence intervals, 95% prediction intervals, and root-mean-squared deviations (RMSD) between the PHXRF and laboratory XRF SC measurements was performed. In addition to an accuracy analysis, a precision analysis comprising standard deviations (σ) between discrete PHXRF measurements was performed.

The one-way ANOVA was conducted with a significance level, α , of 0.05, in which the P-value of the data set would have to be less than or equal to in order to prove that differences between data sets are statistically significant. A regression analysis was used in order to determine the relationship between the PHXRF SC measurements and laboratory XRF SC measurements, where a 1:1 line indicates perfect agreement between the two methods. The slope and intercept of the linear regression equations provide insight as to whether PHXRF over or under predicts the amount of various chemical additives in the stabilized soil samples relative to the laboratory XRF measurements. The r^2 indicates how close the PHXRF SC measurements are to the regression line. An r^2 of 1.0 indicates a perfect fit and that all variability of the data are accounted for and explained by the regression equation, while an r^2 of 0.0 indicates the opposite. The 95% confidence interval graphically shows a range that is 95% likely to contain the mean of the PHXRF SC measurements. The 95% prediction interval graphically shows a range that is 95% likely to contain all discrete PHXRF SC measurements. The RMSD represent the sample standard deviation of the difference between laboratory XRF SC measurements and PHXRF SC measurements. A RMSD equal to 0.0 implies that no difference exists between the two data sets. For this research, RMSD was used primarily to determine relative accuracy. For example, a data set with a RMSD of 1.2 is more accurate than a data set with a RMSD of 2.1 because the former is closer to 0.0. The σ is used as a measure of variation between the data set and its mean. It was used to assess the repeatability of PHXRF SC measurements.

Scan Duration

Scan durations evaluated were 30 – 30 seconds, 15 – 45 seconds, 15 – 60 seconds, and 15 – 120 seconds, where the first number indicates the length of phase I scans (i.e. scans for heavy elements, titanium and heavier) and the second number indicates the length of phase II scans (i.e. for light elements like calcium). Scan durations were found to have negligible effects on the precision and accuracy of SC measurements. When controlling for SC, particle size, sample type, soil type, and scan technique, the differences in mean values among data sets were not great enough to exclude the possibility that the differences are due to random sampling variability. These data show that longer scan durations do not yield appreciable benefits in terms of precision or

accuracy and are, therefore, unnecessary. Consequentially, 60 second (30 – 30) scan durations were used for the remainder of the laboratory portion of this research.

Scan Technique

A standard scanning technique was defined as scanning a sample three times in the same place, whereas a quartering scanning technique was defined as dividing a sample into four quadrants, scanning the first quadrant three times, rotating the sample 90 degrees, scanning the second quadrant three times, etc. This technique was used to assess sample homogeneity. Scan technique appears to play a sizable role in the precision of the PHXRF SC measurements but little to no role regarding accuracy.

Despite the notable differences in precision for the two techniques and two devices, the accuracy was only mildly affected for both. An explanation for this phenomenon may be that the footprints of the X-ray beams for the two devices are different. The footprint for the S1 Titan is ellipse shaped and has an area of 15.71 mm². The footprint of the Niton XL3t's X-ray beam, on the other hand, is circular and has an area of 50.27 mm², nearly three times larger. It is likely that measurements taken by the Niton XL3t, therefore, are naturally more of an average of the sample than those of the S1 Titan. These beam footprints can be seen in Figure 2. Since there was no appreciable difference in accuracy, from an efficiency standpoint, a standard scanning technique is more appropriate because it requires four times fewer scans per sample than the quartering technique.



Figure 2: Beam footprint (red portion) of the S1 Titan (left) and Niton XL3t (right) PHXRF devices.

Particle Size

In order to determine the degree of sample preparation necessary to produce accurate PHXRF SC measurements in a variety of soil types, both montmorillonite and kaolinite-based clays were used. All the verification tests were performed with manufactured

clays and known amounts of stabilizer in order to keep variables to a minimum. The montmorillonite clay was Super Gel-X Bentonite (SGB), an absorbent impure bentonite clay, and the kaolinite clay was Old Hickory Clay (OHC). Both soils were mixed with various amounts of traditional stabilizing agents (i.e. lime, Class C fly ash, or CKD) to create 14 mixes with SCs ranging from 0% to 64%. SC was calculated using Equation 1 (Cerato and Miller 2013). These 14 mixes were milled to four different particle diameters to create a matrix of 56 total samples. It is important to note that creating a matrix of samples with different particle sizes is not as straightforward as performing a standard sieve analysis and then using the material retained in each sieve to produce PHXRF samples. Doing so would produce samples that consist of different proportions of coarse and fine fractions (e.g. passing No. 4 sample would primarily consist of coarse material and passing No. 200 sample would consist of fine material). These samples would therefore contain different minerals and elements, making it impossible to assess the effects of milling efforts on accuracy. Instead, the mixes in this experiment underwent the following treatment: the mixes were ground using a swing mill until all material passed the largest sieve (i.e. No.4 sieve), a portion of this result was bagged for the Passing No. 4 samples and the remainder underwent further milling until all material passes the next largest sieve (i.e. No. 40 sieve), a portion of this result was bagged for the Passing No. 40 samples, etc. This was completed for sieve sizes of No. 4, No. 40, No. 100, and No. 200, thus making samples of identical minerals and elements but different particle diameters. These 56 samples of varying SCs and particle diameters were pressed into 56 compacted pellets and 14 loose powder samples. The compacted pellet material was mixed with Binding Agent, an organic compound added to increase cohesion in the soil, and subjected to 25,000 lbs. of pressure for 60 seconds to produce compacted pellet samples. For comparison, 14 loose powder samples were created simply by filling sample cups with various Passing No. 200 materials and securing a piece of boPET film over the opening of the cup with a sample ring. This created a total matrix of 70 samples of varying SCs, particle sizes, and sample types.

Of all of the variables studied in this research, particle size plays the most prominent role in the accuracy of PHXRF SC measurements. As seen in Table 3, significant drops in RMSD and COV_{RMSD} are observed as samples are milled to smaller particle sizes. However, appreciable benefits seemed to level off once samples were reduced past a No. 40 sieve as seen in Figure 3.

Table 2: Effects of particle size on SC STDEV, COV_{STDEV}, RMSD, and COV_{RMSD} for OHC and SGB samples.

PHXRF Spectrometer	Soil Name	Particle Size (Passing Sieve)	n	STDEV (%)	COV _{STDEV}	RMSD (%)	COV _{RMSD}
S1 Titan	OHC	No. 4	280	0.035	0.001	1.234	0.082
S1 Titan	OHC	No. 40	280	0.025	0.001	0.892	0.062
S1 Titan	OHC	No. 100	280	0.024	0.001	0.915	0.077
S1 Titan	OHC	No. 200	240	0.036	0.001	0.905	0.056
Niton XL3t	OHC	No. 4	21	0.064	0.004	2.128	0.080
Niton XL3t	OHC	No. 40	21	0.091	0.004	1.578	0.064
Niton XL3t	OHC	No. 100	21	0.050	0.002	1.663	0.064
Niton XL3t	OHC	No. 200	18	0.064	0.003	1.794	0.066
S1 Titan	SGB	No. 4	84	0.032	0.001	3.560	0.246
S1 Titan	SGB	No. 40	84	0.039	0.001	2.601	0.190
S1 Titan	SGB	No. 100	84	0.045	0.002	2.323	0.156
S1 Titan	SGB	No. 200	84	0.020	0.001	2.309	0.159
Niton XL3t	SGB	No. 4	21	0.155	0.006	1.607	0.089
Niton XL3t	SGB	No. 40	21	0.075	0.004	1.293	0.057
Niton XL3t	SGB	No. 100	21	0.135	0.006	0.884	0.055
Niton XL3t	SGB	No. 200	21	0.105	0.006	0.984	0.056

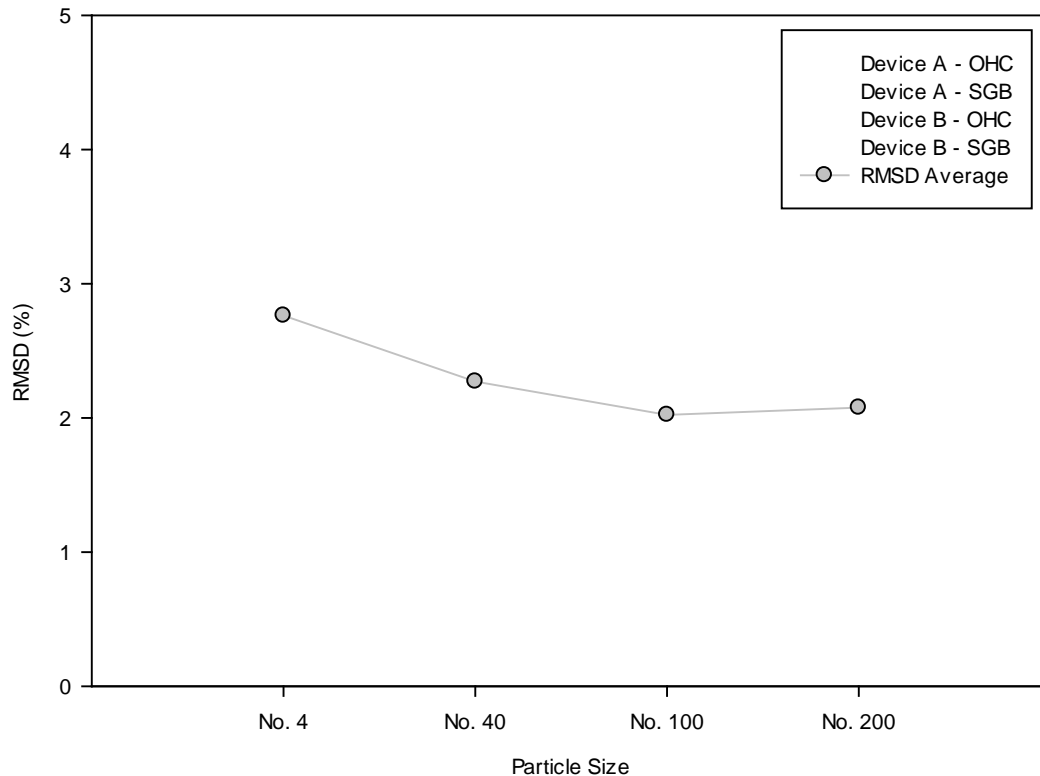


Figure 3. Average RMSD and average COV_{RMSD} as a function of particle size.

The RMSD, or the deviation of the PHXRF SC measurements from the commercial XRF SC measurements, is decreased by 0.342% and 0.334% for the S1 Titan and Niton XL3t, respectively, when the particle size is reduced from passing the No. 4 sieve to passing the No. 200 sieve. The reduction in COV_{RMSD} , or variability of the PHXRF measurements relative to the commercial XRF SC value, confirms that milling samples to smaller particle diameters yield sizable benefits to PHXRF device accuracy. Theoretically, the most accurate samples for all cases should have the smallest particle size (i.e. passing No. 200).

On average in this research, the samples with particle sizes that pass the No. 100 sieve have the smallest RMSD, and samples with particle sizes that pass the No. 200 sieve have the smallest COV_{RMSD} . In terms of field feasibility, however, milling samples to pass the No. 100 and No. 200 sieves is a laborious and time consuming endeavor. This degree of preparation rigor is not practical on site. It may be more conducive to limit milling to passing the No. 40 sieve. As seen in Figure 3, benefits to PHXRF accuracy, both in terms of RMSD and COV_{RMSD} , begin to level off once a sample particle size is reduced passed the No. 40 sieve. For this reason and for the sake of time and cost, it is recommended that all field samples are milled to pass the No. 40 sieve.

Sample Type

The sample types used in this research were pressed pellets and powder samples. The role that sample type plays in the precision and accuracy of PHXRF SC measurements is very pronounced for the kaolinite, OHC samples, but these trends are not confirmed by the bentonite, SGB samples, as seen in Table 3. Effects of sample type on SC STDEV, COV_{STDEV}, RMSD, and COV_{RMSD} for OHC and SGB samples. OHC SC measurement accuracy greatly benefits when the samples are pressed into pellets. The SGB samples tell a different story, however. SGB powder samples produce more accurate SC measurements for the S1 Titan PHXRF spectrometer, and the Niton XL3t SC measurements show no statistical difference between SGB pressed pellet and powder samples. This conflicting data does not allow for a conclusive sample type recommendation to be made. Nevertheless, from a practicality standpoint, powder samples are much more feasible in the field. Creating powder samples in the field only requires a mortar and pestle, a No. 40 sieve, sample cups, and boPET film; whereas, pressed pellet samples require those items plus a hydraulic press, a binding agent, a laboratory scale, and sample caps. The pressed pellets also require approximately 15 minutes to create compared to 3 minutes for the loose powder samples. So in terms of field implementation, it is therefore advantageous to use loose powder samples for PHXRF analysis.

Table 3. Effects of sample type on SC STDEV, COV_{STDEV}, RMSD, and COV_{RMSD} for OHC and SGB samples.

PHXRF Spectrometer	Soil Name	Sample Type	n	STDEV (%)	COV _{STDEV}	RMSD (%)	COV _{RMSD}
S1 Titan	OHC	Pellet	240	0.036	0.001	0.905	0.056
S1 Titan	OHC	Powder	240	0.029	0.001	2.153	0.133
Niton XL3t	OHC	Pellet	18	0.064	0.003	1.794	0.066
Niton XL3t	OHC	Powder	18	0.099	0.005	2.800	0.096
S1 Titan	SGB	Pellet	280	0.020	0.001	2.309	0.159
S1 Titan	SGB	Powder	280	0.035	0.003	1.808	0.145
Niton XL3t	SGB	Pellet	21	0.105	0.006	0.984	0.056
Niton XL3t	SGB	Powder	21	0.068	0.004	0.980	0.051

PHXRF Field Testing

Five different subgrade stabilization sites with different calcium-based stabilizers were located throughout the state of Oklahoma in the spring and summer of 2015. A summary of the sites tested and locations are shown in Table 4.

Table 4: Information on Field Sites.

Site Number	Site Name	Site Location	Site Stabilizer Type and Design Amount
1	I35 Southbound Temporary Collector Road, Norman, OK	35°12'10.22"N, 97°28'48.11"W	CKD: 15%
2	Route 9 and I35 Interchange, Norman, OK	35°11'56.30"N, 97°29'0.42"W	Fly Ash: 16%
3	I35 Southbound – Norman, OK	35°11'53.69"N, 97°28'53.55"W	Portland Cement: 10%
4	Oklahoma State Fairgrounds Expo Center, OKC, OK	35° 28' 12.44"N, 97° 34' 11.31"W	CKD: 15%
5	Subdivision, NW 150 th Street, Edmond, OK	35°37'23.0"N, 97°37'55.3"W	Pretreated Lime (4.5%), with 3% Portland Cement Added

Both in situ and ex situ PHXRF measurements were taken at each site in a grid pattern over a 15.25 meters (50 feet) long by 3.05 meters (10 feet) wide area. In situ measurements are defined in this research as taking surface PHXRF measurements at the grid locations with no sample preparation other than light leveling and tamping of the site surface. Ex situ measurements, on the other hand, are defined as retrieving soil from the subgrade, processing them over a #40 sieve, and placing them in sample cups before scanning them. SC was calculated for both methods using the method presented in Equation 1.

Distances between readings/sample locations were typically 1.5 meters (5 feet) along both the length and width of the grid for a total of 33 locations. Measuring SC in a grid pattern throughout a stabilization project allowed for spatial homogeneity to be assessed. Depth homogeneity was also assessed by retrieving and scanning samples from each of the 33 locations at depths of 0 - 9 and 9 - 12 in. before treatment, and 0 -

3, 3 - 6, 6 - 9, and 9 - 12 after treatment. Additionally, samples from random grid locations were analyzed by commercial XRF laboratory to assess field accuracy of the PHXRF device.

The in situ and ex situ accuracy of the PHXRF SC measurements and site SC homogeneity for five sites were analyzed. All field measurements were taken with the Niton XL3t PHXRF spectrometer. The contour plots of all five sites using the ex situ measurements are presented and highlight the spatial heterogeneity of the stabilization mixing process. Also, the difference in stabilization with depth can be easily seen.

In all five sites, it can be seen that spatial and depth heterogeneity is an issue in subgrade stabilization projects. Ideally, SC should remain constant to a depth of 8 in. and then reduce to zero thereafter, but this was not observed on any of the sites. While SC does decrease significantly below eight inches, there is still a large amount of stabilizer present at this depth on some sites. Typically, the stabilizer amount at some locations in the top 0-3" is well above the amount called for in design.

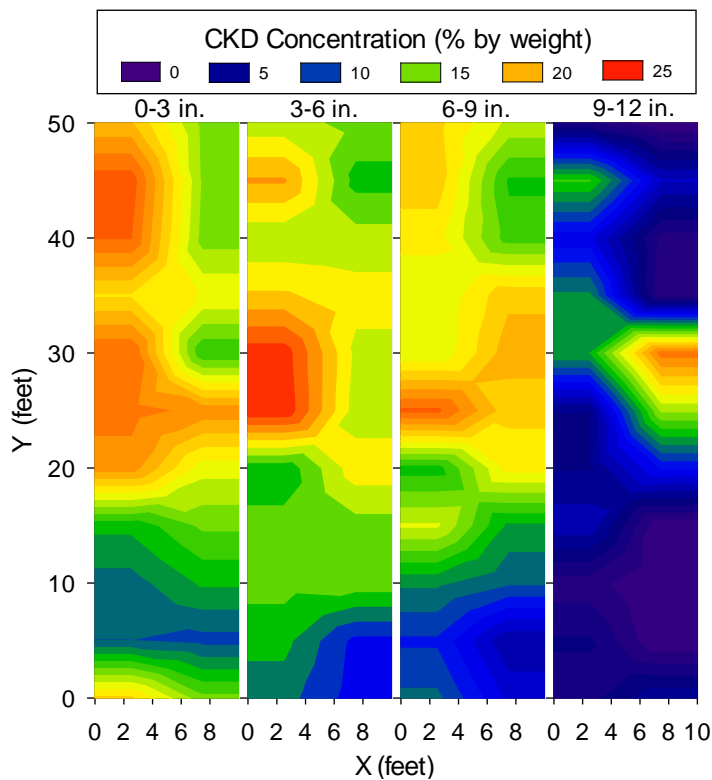


Figure 4: Site 1 Spatial and Depth Distribution of Stabilizer Content (Design CKD 15%)

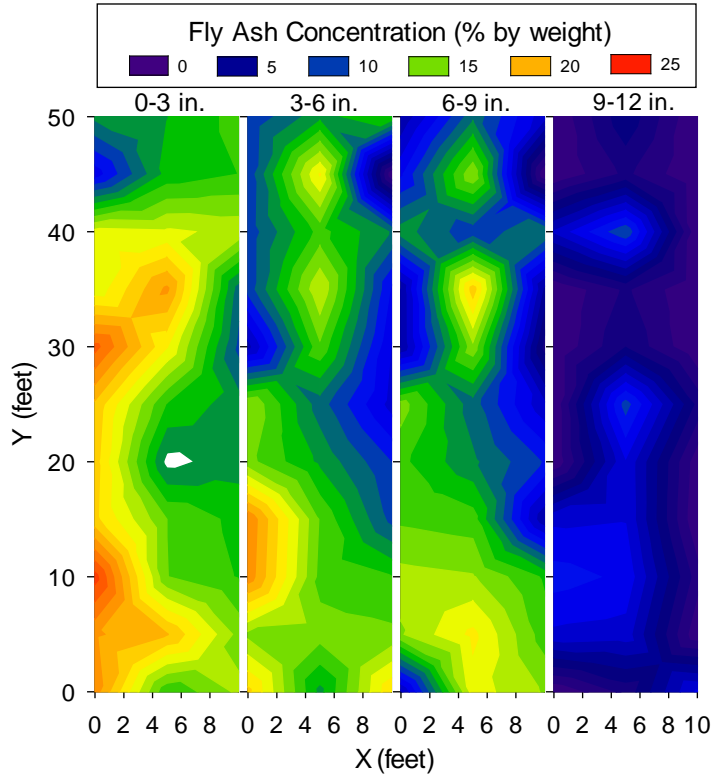


Figure 5: Site 2 Spatial and Depth Distribution of Stabilizer Content (Design FA 16%)

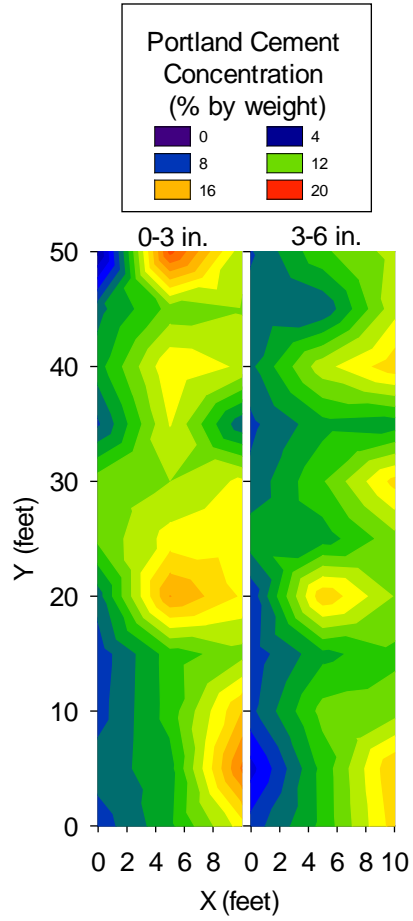


Figure 6: Site 3 Spatial and Depth Distribution of Stabilizer Content (Design PC 10%)

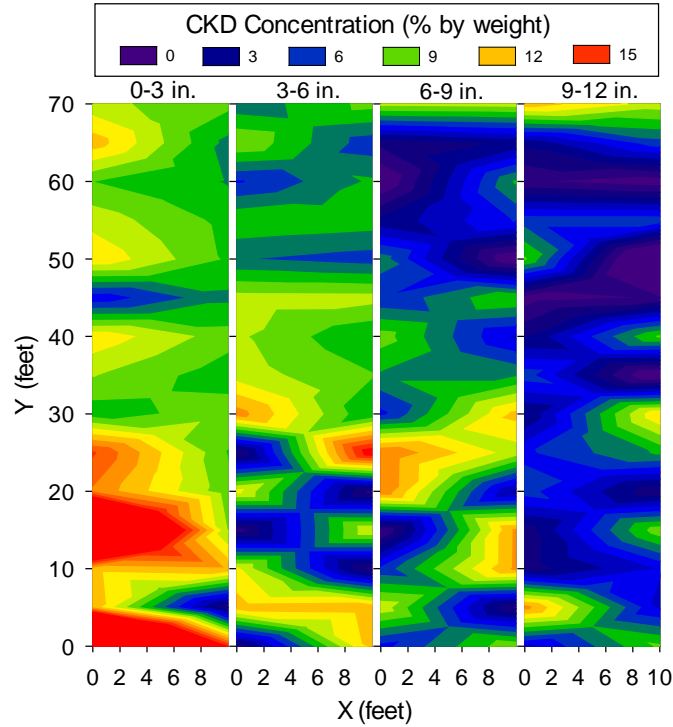


Figure 7: Site 4 Spatial and Depth Distribution of Stabilizer Content (Design CKD 15% - used average “before stabilization” CaO%)

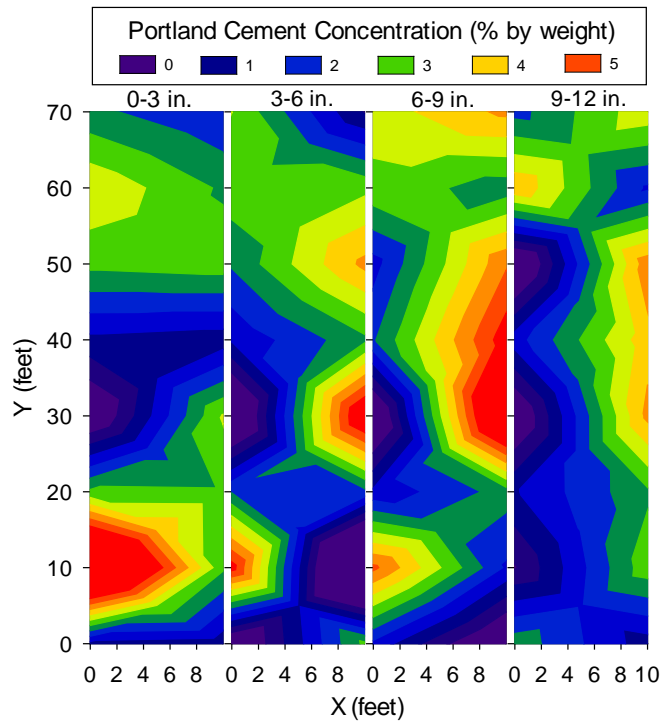


Figure 8: Site 5 Spatial and Depth Distribution of Stabilizer Content (4.5% Lime Pretreatment and 3% PC - used average “after lime pretreatment” CaO%)

A closer look at the first three sites show the extent of the heterogeneity in mixing with depth. Site 1 shows that for the full 8" stabilization depth, the average stabilizer content stayed above the design value of 15%. However, Site 2 shows that the average stabilizer content quickly falls off the design value of 16% to 11% by 8". This may cause problems for the roadway in the future and again provides data showing how effective the PHXRF could be for construction inspection and potential correction of inadequate mixing.

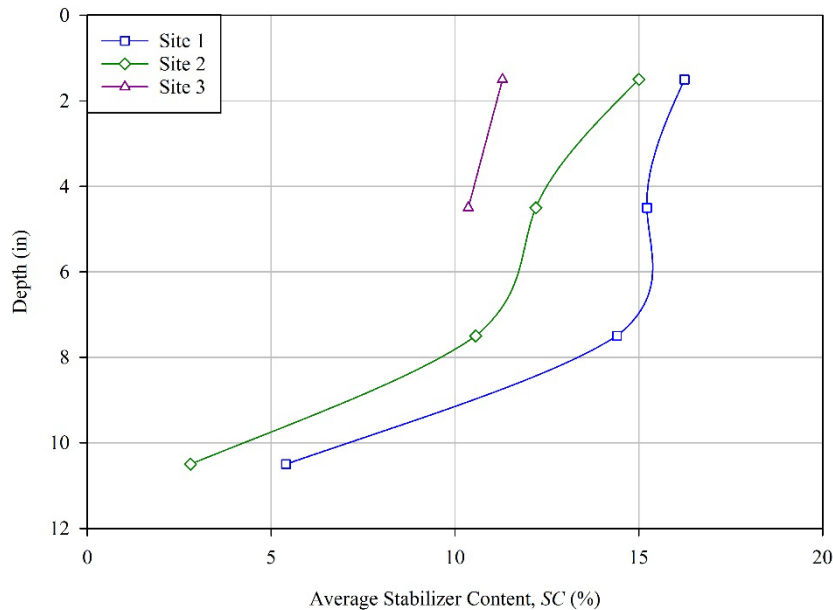


Figure 9: Depth SC heterogeneity for Sites 1-3.

Ex situ PHXRF SC measurements were used to assess the spatial and depth heterogeneity of each site instead of in situ measurements because when the accuracy of both measurements were tested against a commercial XRF laboratory, ex situ measurements were much more consistent. This technique is much more consistent because with ex situ measurements, the soil is sampled from the site at discrete locations, homogenized, processed over a #40 sieve to create a sample with all the same particle size and then pressed into a powder cup for analysis. This creates a more homogenous sample and cuts down on the chance for an extraneous reading on an anomaly in the field, such as a rock or a large clump of pure stabilizer.

To assess the accuracy of ex situ measurements, they were compared to laboratory XRF measurements. The linear regression analysis, as seen in Figure 10, confirms the strong correlations between the two. The deviations between the discrete SC measurements and the one-to-one line suggests poor device accuracy in ex situ conditions; however, the combined trend line fits the data points remarkably well with an r^2 equal to 0.925. This implies that the PHXRF SC measurements can be

mathematically corrected using the equation of the combined trend line to obtain accurate results. This works because the PHXRF gun has to be calibrated to a stabilized soil library and from the laboratory validation studies, corrections to the PHXRF original measurements can easily be made and show quite good measurement accuracy. In the future, it is hoped that stabilized soil specific calibrations can be loaded into the PHXRF gun prior to using in the field so adjustments to the data will not have to be made after the fact. For these reasons, ex situ PHXRF measurements may be an appropriate method for determining SC in subgrade soils.

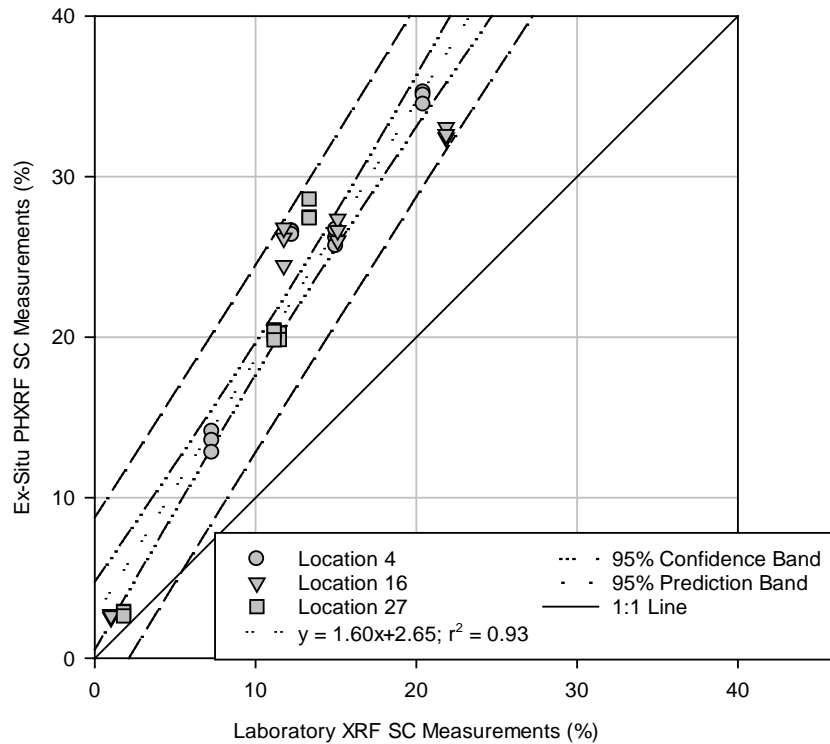


Figure 10. Linear Regression of Site 2 *EX SITU* measurements with the Niton XL3t PHXRF spectrometer.

On the other hand, in situ PHXRF SC measurements differ greatly from measurements made by a commercial XRF laboratory. In fact, there appears to be no relationship between the two. The linear regression analysis seen in Figure 11 confirms the poor performance of the PHXRF during in situ testing. The large areas that lie between the 95% confidence and 95% prediction intervals signify poor precision of the PHXRF measurements, while the deviation from the $y = x$ line proves poor in situ device accuracy. Additionally, the low coefficient of determination, r^2 , suggests that the combined trend line poorly fits the data points. This implies that even when the PHXRF measurements are mathematically corrected using the equation of the combined

trendline, large errors will still be present. It is believed this occurs because when using the PHXRF gun directly on in situ soils, with only a slight tamping to flatten the testing location, the small viewfinder window of the PHXRF may encounter non-homogenous conditions such as clumps of soil, clumps of stabilizer, pebbles or other debris. As manufactured, the window for radiation to leave the gun is very small, therefore, not providing a good indication of conditions even millimeters apart. Because of these sampling and testing issues inherent with simply “pointing-and-shooting” unprocessed and uncontrolled field surface soils, the in situ PHXRF measurements are deemed inappropriate for determining SC in subgrade soils. A certain level of sample preparation is required to measure accurate results. In addition, the in situ measurement only gives an indication of stabilizer content in the upper few millimeters of the subgrade and therefore does not provide a complete picture of SC spatial variability.

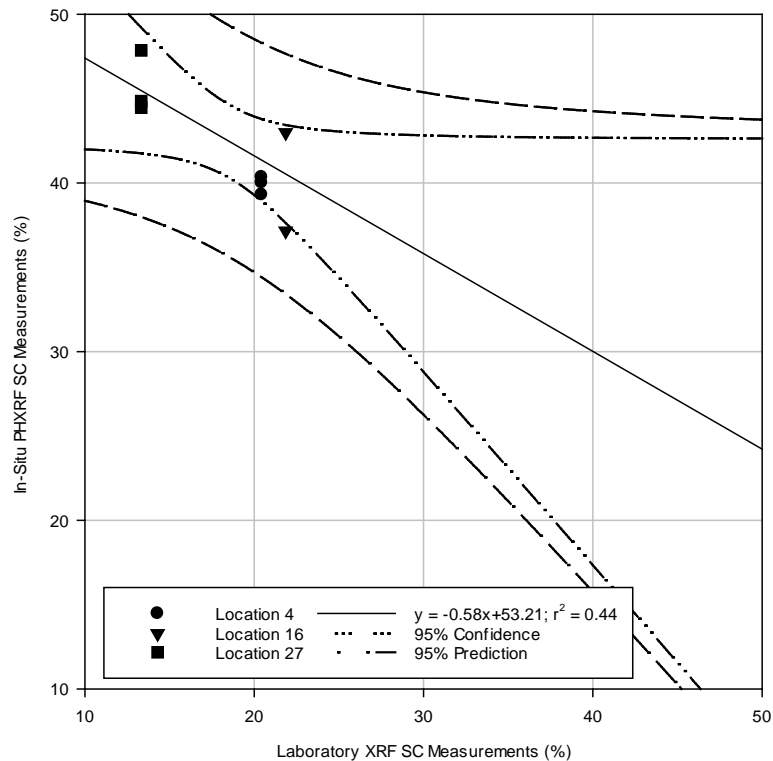


Figure 11: Linear Regression of Site 2 *IN SITU* measurements with the Niton XL3t PHXRF spectrometer.

Laboratory Leaching Tests

If a construction project becomes delayed after a subgrade has been stabilized, and precipitation occurs, the strength of the subgrade may be reduced (Snethen et al.

2008). To quantify the XRF guns ability to measure stabilizer content of treated soils a series of leaching tests were conducted. These tests consist of a matrix of one poorly graded sand (SP), treated with cement kiln dust (CKD), fly ash (FA), and Portland cement (PC). The optimum moisture content of the sand was determined according to ASTM D1557 and was found to be 12.7% at a maximum dry density of 1.79 g/cm³. The stabilizers were mixed with the sand at optimum moisture content. Treatment rates were as follows: CKD = 15%, FA = 16%, and PC = 10%. Tests were conducted at four different curing rates which included 0 day, 1 day, 7 days, and 21 days. Samples were compacted to the maximum dry density using a tamping device and a split mold. The samples were then wrapped in cellophane and placed in a curing room for the desired cure time except for the 0 day sample which was tested immediately after compaction. Test samples were placed in a rubber membrane in a triaxial cell and subjected to flex wall permeameter testing. To simulate various rain water events over a certain time period that would affect the rate of leaching, different amounts of fluid were pushed through the treated sample based on the pore volume of the sample. The volume of water pushed through the sample corresponded with one and three full pore volumes, with one sample using ten pore volumes, which were determined based on mass/volume relationships for the sample at optimum moisture content. XRF was used to determine the variation, if any, of stabilizer content with depth throughout the sample. This was performed to investigate the leaching susceptibility of stabilized soil. In addition, curing time was varied from 0, 1, 7 and 21 days before leaching to see if curing time influences leaching as well.

The percent loss was determined based on an XRF measurement of the stabilizer content in a representative portion of the sample collected prior to forcing fluid through. The stabilizer content was measured again at the end of the test by dividing the testing sample into three sections, top, middle, and bottom and subjecting each to XRF measurement. The end measurement was taken as the average of the readings on the top, middle, and bottom. Each scan for each test section was performed three times and the average was taken as the value for that location. The results of the testing are shown in Table 5.

As can be seen, there was a significant amount of scatter. A positive value indicates that there was a lower stabilizer content in the after permeability test scan, which means that the simulated rainfall tests did flush out some chemical stabilizer. However, the negative values, shown in italics, mean that the stabilizer content in the samples INCREASED after leaching, which cannot occur. Some explanation into this behavior could be that the measurements were so small that they were outside the devices' range of accuracy, therefore any small fluctuations in the XRF scans were not able to be detected. Another reason is that the additive is potentially moving from its original location to other areas in the sample containing high concentrations of material. This would provide slightly larger numbers in the after samples because of how the data were processed by taking the average of three readings. Further tests should be performed to determine exactly how leaching affects stabilized subgrades. It may be useful to increase the hydraulic gradient used in the permeability testing to produce more pronounced leaching in the after samples.

Table 5: Effect of Pore Volume and Curing Time on Stabilizer Leaching as Measured by the XRF.

Stabilizer	Curing Time	Pore Volume	Percent Change (%)
CKD	0	1	-3.29
	1	1	-1.41
	7	1	-0.26
	21	1	0.55
	0	3	-1.19
	1	3	0.13
	7	3	2.44
	21	3	-0.17
	0	10	1.10
Fly Ash	0	1	0.69
	7	1	0.56
	21	1	-0.68
	0	3	1.10
	1	3	-0.30
	7	3	-0.60
	21	3	-1.19
Portland Cement	7	1	-1.10
	7	3	0.20

Conclusions

The purpose of this research was to validate PHXRF on stabilized subgrade projects for construction quality control and geotechnical forensic investigations. This was achieved through two comprehensive rounds of experiments: laboratory testing and field testing. Laboratory testing sought to assess the effects of scan duration, scan technique, sample particle size, and sample type on the precision and accuracy of the SC measurements of the PHXRF devices. Field testing sought to assess how the sampling and testing protocol (e.g., in situ (no soil preparation) and ex situ (some sample preparation)) effected the accuracy of the SC measurements as well as assess relative spatial and depth SC homogeneity of the tested sites. The key findings of this research are as follows:

1. Longer scan durations neither improve nor hinder PHXRF precision and accuracy and are therefore considered negligible. For the sake of efficiency, all PHXRF measurements should be limited to 60 seconds.
2. Significant benefits in terms of PHXRF accuracy are observed when particle sizes are reduced from passing No. 4 to passing No. 40, yet the benefits are less significant when particle sizes are reduced further. Field preparation should be limited to milling samples passed a No. 40 sieve for the sake of feasibility.
3. The relationships between sample type (pressed pellet versus powder) and the precision and accuracy of the PHXRF devices are inconclusive due to conflicting results between OHC and SGB samples.
4. Either a standard scanning technique, where a sample is scanned at the same location three times, or a quartering scanning technique, where a sample is rotated 90° after each scan, may be appropriate for PHXRF SC measurements. Quartering techniques, however, provide a unique opportunity to assess sample homogeneity if the PHXRF in use has a small X-ray beam footprint.
5. The PHXRF device performs poorly in situ (e.g., no sample preparation) when simply used to take measurements directly on the surface of the subgrade. The average STDEV for these measurements is upwards of 2.1%, the RMSD upwards of 24.0%, and no linear relationship between in situ measurements and commercial XRF SC measurements is observed in the data.
6. The PHXRF device performs well ex situ (e.g., sampling and processing soil over a #40 sieve) on representative samples extracted from the subgrade. The linear relationship between ex situ measurements and commercial XRF SC measurements has an r^2 value of 0.925, which suggests that PHXRF measurements can be mathematically corrected to obtain a truer SC value. This also points to the need for developing gun specific calibration libraries designed specifically for stabilized soil testing.
7. Tests on stabilized samples before and after leaching were inconclusive. However, results suggest that for the samples tested the amount of chemical that was potentially lost due to leaching was relatively small and within the accuracy of the PHXRF measurements.
8. PHXRF is a convenient way of gathering data needed to assess the spatial and depth heterogeneity of stabilized subgrade sites.

Cultivating this technology aligns directly with the mission of transportation agencies to develop comprehensive, cost-effective, and imminently implementable solutions to critical infrastructure-related issues facing the transportation systems of the region and the nation. Creating an accurate, portable, and efficient method for determining stabilizer content will enable inspectors to enact improved quality control measures during construction, leading to more reliable and safer roadways. Additionally, this technology will save time and provide more complete data during forensic geotechnical investigations, leading to cost savings and a deeper understanding of stabilization issues. This technology shows great promise in the pursuit of higher quality roadways at levels previously unobtainable.

Recommendations

The XRF technique has the potential to revolutionize the soil-stabilization construction industry. Testing the amount of stabilizer in a subgrade should be a routine part of construction inspection; one made exponentially easier if the measurements can be made in the field and appropriate corrections/modifications immediately made prior to pavement laying. The PI's recommendation to ODOT officials after the 2013 paper was to bag a representative sample of the raw soil, bag a representative sample of the stabilized soil in a few places and then bag a representative sample of the chemical stabilizer and keep those samples in the lab in case future problems arose. After this project, our recommendation is to use the "ex situ" measurement technique by sampling a stabilized section of roadway in a grid pattern and by depth, processing that sample over a #40 sieve to ensure homogeneity in particle size, finger tamping the processed soil into a sample cup, leveling the surface and using the standard sampling technique to take the average stabilizer reading. These readings will have to be corrected with the appropriate regression analyses based on stabilizer type. Further studies should be conducted to further refine this technique by creating a stabilized soil library which is dialed into each PHXRF machine and then implement the calibrated gun on several roadway projects to determine its efficacy. This will alleviate the need to field correct the measurements using the regression line determined during the laboratory validation studies. In addition, research should be conducted on using the PHXRF for determining sulfate content in subgrade soils; this would be an important added benefit of this technology.

References

- Abdelbagi, M., Eltayeb, M.A.H., Rahman, W.S.A. and Elboraie, M.Z. (2011). Source Identification of Airborne Elements in Industrial Area by XRF technique. *Indian Journal of Science and Technology*. Vol. 4, No. 7, pp. 824-827.
- ASTM D3155-11 Standard Test Method for Lime Content of Uncured Soil-Lime Mixtures, ASTM International, West Conshohocken, PA, 2011, <https://doi.org/10.1520/D3155-11>
- ASTM D4609-08 Standard Guide for Evaluating Effectiveness of Admixtures for Soil Stabilization (Withdrawn 2017). ASTM International, West Conshohocken, PA, 2008.
- Baranowski, R., A. Rybak, and I. Baranowska. (2002). "Speciation Analysis of Elements in Soil Samples by XRF." *Polish Journal of Environmental Studies* 11.5. 473-82.
- Cerato, A. and G. Miller. (2013) Determination of Soil Stabilizer Content Using X-ray Fluorescence. *Geotechnical Testing Journal*, Vol. 36, No. 5: 781-785.
- Chakrabarti, S. and Kodikara, J. (2007). Microstructure and its Relationship to Some Material Properties of Cementitiously Stabilized Crushed Basaltic Rock. *Road and Transport Research*. Vol. 16, No. 2, pp. 3-18.
- Chou, J., Elbers, D., Clement, G. Bursavich, B., Tian, T. Zhang, W. Yang, K. (2010). In situ monitoring (field screening) and assessment of lead and arsenic contaminants in the greater New Orleans area using a portable X-ray fluorescence analyser. *Journal of Environmental Monitoring*. Vol. 12, No. 9, pp. 1722-1729.
- Constantinescu, Bogdan, Angela Vasilescu, Martin Radtke, and Uwe Reinholz. (2010). Micro-SR-XRF Studies for Archaeological Gold Identification-The Case of Carpathian Gold and Romanian Museal Objects. *Applied Physics A: Materials Science & Processing*. May 99.2: pp. 383-89.
- Eades, J.L. and Grim, R.E. (1966). A quick test to determine requirements for lime stabilization. *Highway Research Board Bulletin*. Vol. 139. pp. 61-72.
- Elam, W.T., Adams, J.W., Hudson, K.R., Eng, D., Robitaille, G. and Aggarwal, I. (1997a). Field Demonstration of the SCAPS XRF Metals Sensor. Fifth Symposium on *Field Screening Methods for Hazardous Waste and Toxic Chemicals*, Air and Waste Management Assoc, Las Vegas, NV, Jan. 1997. (Abstract).
- Elam, W.T., Adams, J., Hudson, K.R., McDonald, B., Eng, D., Robitaille, G. and Aggarwal, I. 1997b. Field Demonstration of the SCAPS XRF Metals Sensor. Report to the Department of Defense, Naval Research Lab. <http://www.dtic.mil/cgi-bin/GetTRDoc?AD=ADA348516>

- Esser, K.B., Bockheim, J.G. and Helmke, P.A. (1992). Mineral Distribution in Soils formed in the Indiana Dunes, USA. *GeoDerma*. Vol. 54, pp. 91-105.
- Gunter, M., Bailey, D.G., Goodale, N., Coles, M. and Kuijt, I. (2010). Portable XRF analysis of Gravestones composed of fine-grained metamorphic and sedimentary rocks from early medieval Ireland. Geological Society of America, 2010 Annual meeting, Denver, CO, USA. Abstracts with Programs. Vol. 42, No. 5, pp. 577.
- Hilt, G.H. and Davidson, D.T. (1960). Lime Fixation in Clayey Soils. Highway Research Board Bulletin. Vol. 262. pp. 20-32.
- Imanishi, Y., Bando, A., Komatani, S., Wada, S-I and Tsuji, K. (2010). Experimental Parameters for XRF Analysis of Soils. International Centre for Diffraction Data. pp. 248-255. ISSN 1097-0002.
- Markowicz, A. (2011). An overview of quantification methods in energy-dispersive X-ray fluorescence analysis. *Pramana Journal of Physics, Indian Academy of Sciences*. Vol. 76, No. 2, pp. 321-329.
- Maruyama, Y., Ogawa, K., Okada, T. Kato, M. (2008). Laboratory experiments of particle size effect in X-ray fluorescence and implications to remote x-ray spectrometry of lunar regolith surface. *Earth Planets Space*, Vol. 60. Pp. 293-297.
- Melquiades, F. L., and C. R. Appoloni. (2004). Application of XRF and Field Portable XRF for Environmental Analysis. *Journal of Radioanalytical and Nuclear Chemistry*. Vol. 262, No.2, pp. 533-41.
- Morgenstern, Peter, Lutz Bruggemann, Ralph Meissner, Juliane Seeger, and Rainer Wennrich. (2010). Capability of a XRF Method for Monitoring the Content of the Macronutrients Mg, P, S, K and Ca in Agricultural Crops. *Water, Air, & Soil Pollution*. Vol. 209. pp. 315-22.
- Oklahoma D.O.T. (2009) OHD L-50 Soil Stabilization Mix Design Procedure, July 28, 2009.
- Oklahoma D.O.T. (2009) OHD L-51 Soil Modification Mix Design Procedure, July 28, 2009.
- Rogers, C.D.F and Glendinning, S. (1996). The role of lime migration in lime pile stabilization of slopes. *The Quarterly Journal of Engineering Geology*. Vol. 29, No. 4, pp. 273-284. doi:<http://dx.doi.org/10.1144/GSL.QJEGH.1996.029.P4.02>
- Shefsky, S. (1997). Comparing Field Portable X-ray Fluorescence (XRF) to Laboratory Analysis of Heavy Metals in Soil. *Proceedings of the International Symposium of Field*

Snethen, D.R., Miller, G.A. and Cerato, A.B. (2008). Evaluation and Field Verification of Strength and Structural Improvement of Chemically Stabilized Subgrade Soil. Technical Report. Oklahoma Department of Transportation, Oklahoma City, OK.

Starr, M. and Lindroos, A-J. (2006). Changes in the Rate of Release of Ca and Mg and normative mineralogy due to weathering along a 5300-year chronosequence of boreal forest soils. *GeoDerma*. Vol. 133, pp. 269-280.

Swift, R. P. (1995). Evaluation of a Field-Portable X-ray Fluorescence Spectrometry Method for Use in Remedial Activities. *Spectroscopy*. Vol. 10, No. 6, pp. 31-35.

Weindorf, D., Rolong, N., Ferrell, R., Allen, B.L., Hudnall, W., etc. (2008). Evaluation of Portable X-ray Fluorescence for Gypsum Quantification in Soils. Geological Society of America. Page. 469.

Weindorf, D., Zhu, Y., Ferrell, R., Rolong, N., Barnett, T., Allen, B.L., Herrero, J. and Hudnall, W. (2009). Evaluation of portable x-ray fluorescence for gypsum quantification in soils. *Soil Science*, Vol. 174, No. 10, pp. 1-7.

Zawisza, B. and R. Sitko. (2006) "Determination of Trace Elements in Suspension and Filtrates of Drinking and Surface Water by Wavelength-Dispersive X-ray Fluorescence Spectrometry." *Analytical and Bioanalytical Chemistry*, Vol. 384 1600-1604.