

FINAL REPORT ~ FHWA-OK-22-05

USING X-RAY FLUORESCENCE TO ASSESS SOIL SUBGRADE STABILIZATION COMPETENCY DURING CONSTRUCTION INSPECTION

**Amy B. Cerato, Ph.D., P.E.,
Gerald A. Miller, Ph.D., P.E.,
Kwestan Salimi, Ph.D. Candidate
Michelle Basham, Ph.D. Candidate**

**School of Civil Engineering and Environmental Science (CEES)
The University of Oklahoma
Norman, Oklahoma**

April 2022



OKLAHOMA
Transportation

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USING X-RAY FLUORESCENCE TO ASSESS SOIL SUBGRADE STABILIZATION COMPETENCY DURING CONSTRUCTION INSPECTION

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Submitted to:

Office of Research and Implementation
Oklahoma Department of Transportation

Submitted by:

Amy B. Cerato, Ph.D., P.E.,
Gerald A. Miller, Ph.D., P.E.,
Kwestan Salimi, Ph.D. Candidate
Michelle Basham, Ph.D. Candidate
School of Civil Engineering and Environmental Science (CEES)
The University of Oklahoma



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16. ABSTRACT A large portion of transportation corridor projects use lime and other calcium-based stabilizers to reduce soil plasticity, increase shear strength, reduce compressibility, and reduce volume changes when subjected to variations in water content. While design and construction practices for subgrade stabilization have been standardized, there is no extant quality control measures, particularly measures that are timely, cost effective, and accurate. Therefore, this study was undertaken to evaluate the ability of portable handheld X-ray fluorescence (PXRF) to detect calcium stabilizers in soil samples. The accuracy of Whole Rock XRF (WXRF) was evaluated and used to verify a variety of PXRF measurement techniques, including scan duration, particle size, and sample type. Additionally, the viability of PXRF in measuring soil sulfate content was investigated. It was concluded that the WXRF method is highly accurate in detecting both calcium and sulfate in soils, with average magnitude of deviation between WXRF-determined stabilizer content and actual stabilizer content of 0.3%. While the PXRF method found to be less accurate than WXRF, the average magnitude for clay samples was 2.1% and 10.6% for sand samples. Moreover, the existing calibration libraries do not require slope correction for calcium contents in lower ranges, but do not accurately measure calcium content in higher ranges. The calibration libraries for sulfate detection are able to accurately detect sulfate contents in the range of 0 to 8%, but require individual calibration coefficients.					
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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
cu ft	cubic feet	0.028	cubic meters	m ³
cu yd	cubic yards	0.765	cubic meters	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	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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G. Scott Garland, Jr., P.E., Geotechnical Branch Manager

Matt Romero, P.E., Materials Division Engineer

ODOT Division 3

Luis D. Malave, P.E., Purcell Resident Engineer

Matthew Helton, P.E., Weewoka Resident Engineer

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Christopher J. Fuhrmann, P.E., Ardmore Resident Engineer

Colton Roberts, P.E., Duncan Resident Engineer

Table of Contents

Acknowledgments.....	vi
Table of Contents.....	vii
List of Tables	viii
List of Figures	ix
Chapter 1: Introduction	12
1.1 Problem Statement.....	12
1.2 Background	13
1.3 Objectives and Tasks	13
Chapter 2: Testing Optimization.....	14
2.1 Materials	14
2.2 Soil Sample Preparation.....	15
2.3 Whole Rock XRF (WXRF)	16
2.4 Portable Handheld XRF (PXRF)	16
Chapter 3: Whole Rock XRF Results	17
3.1 Influence of Additive Type.....	18
3.2 Influence of Soil Type	20
Chapter 4: PXRF Results	22
4.1 Influence of Additive Type.....	23
4.2 Influence of Soil Type	25
4.3 Influence of Sample Preparation and Scanning Procedure.....	28
4.3.1 Preparation using Pressed Pellet vs Powder	28
4.3.2 Particle Size	30
4.3.3 Scan Type and Scan Duration.....	32
Chapter 5: Investigation of Various PXRF Libraries in Detecting Stabilizer Content.....	32
5.1 Laboratory Mixed Samples.....	32
5.2 Field Samples.....	41

Chapter 6: Standard Sampling and Testing Procedure and Contractor Specifications.....	45
6.1 Sampling and Testing Procedure	45
6.2 Proposed Pay Deduction Scale	50
Chapter 7: Investigation of Various PXRF Libraries in Detecting Sulfate Content.....	52
Chapter 8: Recommendations and Conclusions	56
8.1 Recommendations.....	56
8.2 Conclusions.....	57
References	59

List of Tables

Table 1. Soil Properties.....	15
Table 2. Average influence of additive type on WXRF: Statistical analysis results.	19
Table 3. Standard Deviation of influence of additive type on WXRF: Statistical analysis results	19
Table 4. Coefficient of deviation of influence of additive type on WXRF: Statistical analysis results	20
Table 5. Average influence of soil type on WXRF: Statistical analysis results	21
Table 6. Standard deviation of influence of soil type on WXRF: Statistical analysis results	21
Table 7. COV of influence of soil type on WXRF: Statistical analysis results	22
Table 8. Average influence of additive type on PXRF: Statistical analysis results.....	24
Table 9. Standard deviation of influence of additive type on PXRF: Statistical analysis results.	24
Table 10. COV of influence of additive type on PXRF: Statistical analysis results	25
Table 11. Average of influence of soil type on PXRF: Statistical analysis results	26
Table 12. Standard deviation of influence of soil type on PXRF: Statistical analysis results	26
Table 13. COV of influence of soil type on PXRF: Statistical analysis results.....	26
Table 14. Statistical analysis results for SS	27
Table 15. Average of influence of sample preparation on PXRF: Statistical analysis results.....	28
Table 16. Standard deviation of influence of sample preparation on PXRF: Statistical analysis results	29
Table 17. COV of influence of sample preparation on PXRF: Statistical analysis results.....	29

Table 18. Average of influence of particle size on PXRF: Statistical analysis results	31
Table 19. Standard deviation of influence of particle size on PXRF: Statistical analysis results	31
Table 20. COV of influence of particle size on PXRF: Statistical analysis results	31
Table 21. Bentonite and Class C Fly Ash mix design matrix	32
Table 22. Bentonite and Cement Kiln Dust mix design matrix	33
Table 23. Bentonite and Portland Cement mix design matrix	33
Table 24. Bentonite and Lime mix design matrix	34
Table 25. Kaolinite and Class C Fly Ash mix design matrix	34
Table 26. Kaolinite and Cement Kiln Dust mix design matrix	34
Table 27. Kaolinite and Portland Cement mix design matrix	35
Table 28. Kaolinite and Lime mix design matrix	35
Table 29. Conversion between CaO and Ca and Ca to CaO.	36
Table 30. The Field Sites, Locations, and Design Percentage	42
Table 31. Field site stabilizer content values using GeoMine (Sites 1 – 5)	43
Table 32. Field site stabilizer content values using GeoMine (Site 6)	44
Table 33. Proposed pay factors for calcium-based stabilization projects: CKD, FA, PC acceptance schedule	51
Table 34. Proposed pay factors for calcium-based stabilization projects: Lime acceptance schedule	51
Table 35. Conversions from CaO to Ca and SO ₃ to SO ₄ to determine sulfate (CaSO ₄) content of soils.	52
Table 36. Soil mix design for reference standards to determine sulfate content using PXRF.	52

List of Figures

Figure 1. Whole Rock XRF analysis: a) measured SC _w data versus SC _a data; b) the distribution of the deviation between SC _w and SC _a	18
Figure 2. Influence of additive type on WXRF: a) the deviation between SC _w and SC _a versus SC _a ; b) $\text{abs}(\Delta\text{SC}_{\text{wa}})/\text{SC}_{\text{a}}$	19
Figure 3. Influence of soil type on WXRF: a) the deviation between SC _w and SC _a versus SC _a ; b) $\text{abs}(\Delta\text{SC}_{\text{wa}})/\text{SC}_{\text{a}}$	21

Figure 4. PXRF analysis: a) measured SC _p data versus SC _w data; b) the distribution of the deviation between SC _p and SC _w	23
Figure 5. Influence of additive type on PXRF: a) the deviation between SC _p and SC _w versus SC _w ; b) abs (ΔSC _{pw})/SC _w	24
Figure 6. Influence of soil type on PXRF: a) the deviation between SC _p and SC _w versus SC _w ; b) abs (ΔSC _{pw})/SC _w	26
Figure 7. PXRF analysis for SS: a) the deviation between SC _p and SC _w versus SC _w ; b) abs (ΔSC _{pw})/SC _w	27
Figure 8. Influence of sample preparation on PXRF: a) the deviation between SC _p and SC _w versus SC _w ; b) abs (ΔSC _{pw})/SC _w	29
Figure 9. Influence of particle size on PXRF: a) the deviation between SC _p and SC _w versus SC _w ; b) abs (ΔSC _{pw})/SC _w	30
Figure 10. Comparison between PXRF and WXRF measurements of Calcium (Ca).	37
Figure 11. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO). ...	37
Figure 12. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO) of the chemical stabilizers.	38
Figure 13. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO) of the chemical stabilizers with less than 45% calcium contents.....	39
Figure 14. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO) of the chemical stabilizers with slope coefficients to both the GeoExplore and GeoMine libraries for the Portland Cement, Cement Kiln Dust and Fly Ash stabilizers.....	40
Figure 15. Calculated SC of all mixed samples, including PC, Lime, FA, and CKD stabilized soils, without calibration coefficients.....	41
Figure 16. Map of Field Testing Locations	42
Figure 17. Variation of PC content in 10 ft x10 ft test section of Wayne Payne site determined by PXRF measurement. (Design PC 3%).	45
Figure 18. Specimen preparation: a) Place cap ring over foil; b) Ensure cap ring is fully on; c) Measure from film end; and d) Mark with pen.....	47
Figure 19. Specimen preparation: a) Press the powder with a dowel; b) Place paper circle on top of sample.....	48

Figure 20. Specimen preparation: a) Place cotton ball on top of paper; b) Fit cotton into remaining space.....	49
Figure 21. Sample preparation: a) Place lid on top of cotton; b) Finished samples	50
Figure 22. Standard, noncalibrated PXRF Results vs Mixture Percentages.....	54
Figure 23. Calibrated Reference Curves using S1 Titan PXRF (top full scale and bottom figure showing only 0-2%)......	55

Chapter 1: Introduction

1.1 Problem Statement

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 such as lime render highly plastic expansive soils non-plastic and non-expansive. While the design and construction procedures for subgrade stabilization are somewhat standard, there are no viable quality control measures, including construction inspection protocols or techniques, available to determine the actual amount of stabilizer in the soil nor to assess the spatial or depth distribution through the stabilized layer. Some subgrade specifications reference either a dye indicator test or a titration method as a possible quality control method. However, the dye indicator test (i.e., Phenolphthalein Test) only detects the presence of a stabilizing agent, not the amount (National Lime Association 2004). The titration method (ASTM D3155-11), while capable of producing quantitative measurements, is complex, requires the user to handle harsh chemicals, mix upwards of six reference solutions, and has questionable accuracy due to a large operator bias (Cerato and Miller, 2013; ASTM D3155-11). Additionally, this method was developed only for lime treated soils. The limits of both the dye indicator and titration methods render the development of a new, more accurate, and more repeatable quality control technique necessary.

Through previous research (Cerato and Miller 2013), 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. 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 seeks to further validate this technique by increasing the accuracy of the device with the creation of a calibration library of stabilized soils with the support of a manufacturer. Once the stabilized soil-specific calibration of the field employed XRF (PFXRF) is complete, an implementation plan for construction quality control will be rolled-out. Previous work of the PIs in this regard shows that the technique has promise and can clearly show the

non-homogenous mixing that occurs in the field. The importance of an adequately stabilized subgrade cannot be overstated and the PFXRF has the potential to avoid roadway damage by helping construction officials achieve a more uniform and better behaving pavement system.

1.2 Background

X-ray fluorescence (XRF) spectrometry is an established analysis technique used to determine the elemental makeup of a material. It has been studied for over 100 years and has been used in a wide range of applications, including environmental analyses of water quality, air quality, and lead contamination (Abdelbagi et al., 2011; Binstock et al., 2008; Kim et al., 2007; Zawisza and Sitko, 2006); pharmaceutical analyses of drug impurities, catalyst residues, and vitamin extraction (Moradi et al., 2015; Ortiz et al., 2012; Arzhantsev et al., 2011; Marguá et al., 2009); archeological analyses of obsidian (Frahm 2013; Forster and Grave, 2012; Millhauser et al., 2011); consumer goods analyses of FDA-regulated products and household items (Sun et al., 2013; Kulikov et al., 2012; Palmer et al., 2009; Rourke et al. 2016); and soil analysis for characterization of heavy metals in soils (Bolan et al., 2014; Duan et al., 2018; Ju et al., 2019; Li et al., 2020). Cerato and Miller (2013) found that a laboratory-based XRF procedure produces on average, a 1:1 correlation between measured and mixed stabilizer contents (SCs) with good accuracy. Laboratory XRF is certainly a viable option for subgrade stabilization investigations; however, turnaround time (2+ weeks) is an obstacle to implementation for quality control applications (Cerato and Miller, 2013).

Portable X-ray fluorescence spectrometry (PXRF) has been a popular option for soil analysis providing the benefits of accurate, non-destructive analysis capabilities with the convenience of portability, time savings, and reduced sample transport and storage costs (e.g., Weindorf et al., 2012; Parsons et al., 2013; Weindorf et al., 2015). Capability of PXRF in measuring the elements with atomic weights greater than 12 (e.g., Weindorf and Chakraborty, 2016; Chakraborty et al., 2017; Teixeira et al., 2018) has recently led researchers to use PXRF for differentiation of land use types (e.g., Chakraborty et al., 2019; Sun et al., 2020; Benedet et al., 2020).

1.3 Objectives and Tasks

The primary objectives of the research project were: 1) To refine and optimize sampling and testing PXRF protocols on five ODOT construction stabilization projects. 2) To refine and record the most efficient, yet accurate, sampling and testing protocols for assessing subgrade stabilization content and distribution and optimize the sampling and soil processing protocols for

efficiency and accuracy in the field. 3) Investigate the detection accuracy of PXRF on soil sulfate. 4) To provide recommendations if this technology is to be implemented by industry including contractors and construction inspectors.

Results of this research project 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. To achieve the project objectives, the following tasks have been completed during the first year of the project, which support the long-term goal:

1. The accuracy of Whole Rock XRF (WXRF) method in determining stabilizer content was evaluated.
2. The viability of Portable Handheld XRF (PXRF) method in determining stabilizer content was investigated.
3. The influence of independent variables (i.e., scan durations, scan techniques, maximum particle sizes, and sample types) on the accuracy and precision of the PXRF was studied.
4. The materials used in this research, soil sample preparation, and methods to determine the stabilizer contents were determined.
5. The field sites and their location were identified with assistance of ODOT personnel.
6. The viability of Portable Handheld XRF (PXRF) method in determining soil sulfate content was investigated.
7. A standard sampling and testing procedure and pay deduction scale to be used on stabilization projects was proposed.

Chapter 2: Testing Optimization

2.1 Materials

In this study, three soil types, with properties summarized in Table 2, were used. These soils include a Kaolinite soil from Hickory, Kentucky called Old Hickory Clay (OHC); an adsorbent impure bentonite from Titan Industries called Super Gel-X Bentonite (SGB); and Stephenville sand, a silty sand (SS) from Texas. Four different chemical additives used in this study were

Hydrated Lime (HL), Cement Kiln Dust (CKD), Fly Ash Class C (FA), and Portland Cement (PC).

Table 1. Soil Properties

Soil types	Passing #10 (%)	Passing #40 (%)	Passing #200 (%)	LL (%)	PI
OHC	100	100	98.5	70	32
SGB	100	100	70	283.2	39.3
SS	100	99.1	27.7	NP	NP

2.2 Soil Sample Preparation

First, soils were dry mixed with stabilizers to reduce the amount of stabilizer agglomerations that would form after water was added. After the addition of the water, samples were mixed for five minutes using a mechanical blender with a wire whisk attachment. SGB required significantly more water because it is a highly expansive montmorillonite clay with more absorptive properties. After blending, the mixes were air dried for two to four weeks.

Once dry, the soil was processed over a #40 sieve and approximately 50 g of each mix was mailed to ALSglobal where it was subjected to a “Whole Rock Analysis.” CaO was used as the elemental compound to calculate the percentage of chemical additives in each sample. Referring to Equation 1, the percentage of chemical additive in a stabilized soil sample equals the increase in CaO (% of total dry weight) between the treated and untreated soil divided by the difference of CaO in the additive and untreated soil (Cerato and Miller, 2013).

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

where: SC is the chemical stabilizer content in the chemically stabilized soil sample (% of total dry weight), CaO_f is the amount of CaO measured by PXRF in the chemically stabilized soil sample (%), CaO_0 is the amount of CaO measured by PXRF in the untreated soil sample (%), CaO_{CA} is the amount of CaO measured by PXRF in the chemical additive (%).

To investigate the impact of soil particle size on the accuracy of PXRF measurements, OHC and SGB clays were milled to pass the No. 4, No. 40, No. 100, and No. 200 sieves (4.76 mm, 0.425 mm, 0.149 mm, and 0.074 mm, respectively). A portion of these samples were pressed into compacted pellets and a portion of the passing No. 200 sieve samples were used to create powder samples. The compacted pellet material was mixed with binding agent, an organic compound

added to increase cohesion in the soil, and then subjected to 25,000 lbs. of pressure for 60 seconds. The loose powder samples were created simply by filling sample cups and securing a piece of Prolene film over the opening of the cup with a sample ring. It is very important to fill the sample cups completely to the top with sample material to avoid the development of a gap between the surface of the material and the film. It has been shown that a gap adversely affects the accuracy of the PXRF measurements.

2.3 Whole Rock XRF (WXRF)

The samples were sent to a commercial laboratory and subjected to Whole Rock XRF (WXRF) analysis. The stabilizer content determined by WXRF (SC_w) for each sample was compared with the actual stabilizer content (SC_a) added during sample preparation. While comparing SC_w and SC_a data, a linear regression analysis was performed to determine the suitability of a linear function to model the data. The accuracy of the WXRF procedure in determining SC_w is reflected by the slope, intercept, and coefficient of determination, R^2 . Higher accuracy is associated with an intercept that approaches zero, a slope that approaches one, and the coefficient of determination, R^2 , approaching one. Moreover, the accuracy of the measurements was further assessed by calculating the deviation between the SC_w and SC_a . The distribution of the calculated deviation was then graphed. Standard deviation ($STDEV$) and coefficient of variation of the standard deviation (COV_{STDEV}) were used as the statistical methods to analyze the deviation data. $STDEV$ is a statistic used to quantify the variation between each SC_w and the mean SC_a . High precision is indicated by a $STDEV$ that is close to zero. COV_{STDEV} is used to assess the dispersion of the SC_w to the mean SC_a , defined as the ratio between the $STDEV$ and the mean. High precision is indicated by a COV_{STDEV} close to zero.

2.4 Portable Handheld XRF (PXRF)

The PXRF device used for this research was the S1 Titan model 600. The accuracy of the PXRF method was evaluated by comparing the PXRF stabilizer contents (SC_p) to the SC_w values obtained by WRXF analysis on the same samples. The reason the SC_w values were taken as the “true” values, was due to the fact that for samples obtained in the field, that are the subject of an ongoing study, the only way to determine a “true” value for comparison to PXRF determined values was to use another, more accurate measurement technique. The WXRF method has proven to be very accurate, as discussed later, and thus, has been adopted to establish “true” values of stabilizer content to which all PXRF determined SCs are compared. The influence of

independent variables including scan duration, scan technique, particle size, and sample type (powder and pellet) on the accuracy of the PXRF measurements were also assessed.

The S1 TITAN is equipped to perform dual phase measurements; phase I detects the light elements of Mg, Al, and Si, and phase II detects non-light elements. Since calcium is the element central to this research, Phase II scan durations were varied to longer lengths. The following scan durations were assessed: 30 - 30, 15 - 45, 15 - 60, and 15 - 120, where the first number represents the length of Phase I scan in seconds and the second number represents Phase II. Scan technique was assessed by conducting standard scans (i.e. scanning a sample three times in the same place) and quartering scans (i.e. scanning the first quadrant three times, rotating it 90°, scanning the second quadrant three time, rotating it 90°, etc.). The same statistical methods discussed in the previous section were followed to evaluate the accuracy of the PXRF device by comparing measured SC_p .

Chapter 3: Whole Rock XRF Results

Fig. 1 (a) shows the WXRF data (SC_w) plotted against the actual data (SC_a), representing three different soil types and four different additive types. As shown, data plot very close to a 1:1 line with intercept approaching zero at 0.054 %, the slope close to one at 0.985 and R^2 close to one at 0.999. This suggests that the WXRF method is quite accurate in determining stabilizer content. Fig. 1 (b) illustrates the distribution of the SC_w deviation from the actual data; revealing that most of the deviations are between 0% and 0.2% (percent of total dry weight), and that the deviations are roughly normally distributed around this range (except for the outlier at -3 to -3.2) (Fig. 1b). This indicates that experimental errors are random, and no systematic errors have occurred. These observations mean that loosely, the majority of the WXRF-determined values of SC_w should be within 0.2% of the actual values (e.g., if actual lime $SC=4.0\%$, SC_w should be 3.8% to 4.2%).

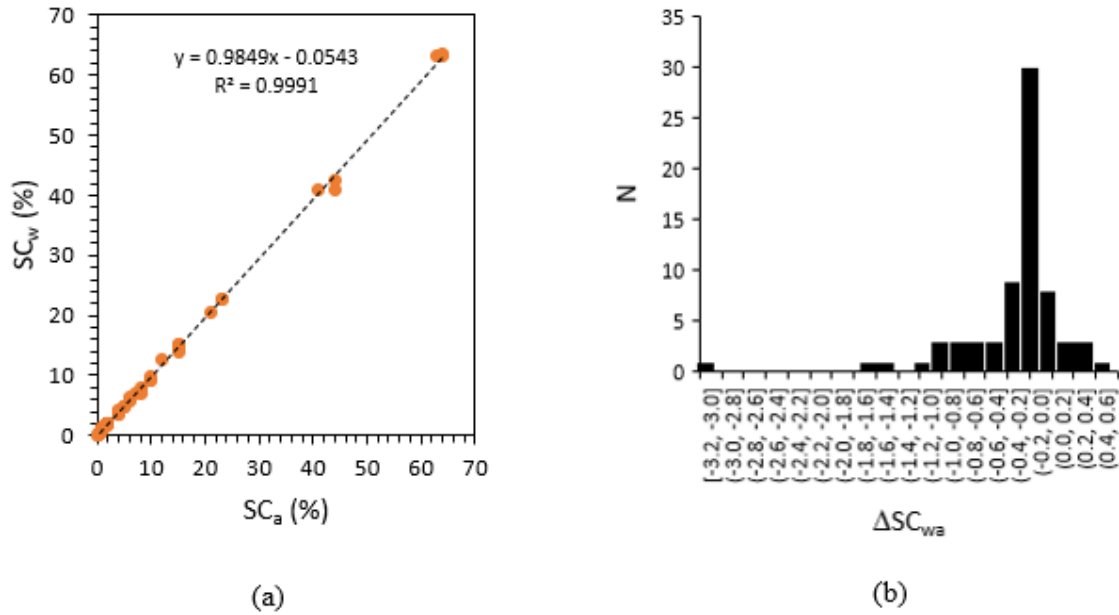


Figure 1. Whole Rock XRF analysis: a) measured SCw data versus SCa data; b) the distribution of the deviation between SCw and SCa

3.1 Influence of Additive Type

The influence of additive type on stabilizer contents determined through the WXRF method is illustrated in Fig. 2 and in Table 2, which summarize the deviations (ΔSC_{wa}) between SC_w and SC_a . In Fig. 2(a) and Table 2, it can be observed that the average deviation is slightly below zero for most of the additives, with the exception of lime, and is greatest for the fly ash. The latter observation is due to the larger deviations observed for two of the fly ash samples near the SC_a content of 40%, which appear to be outliers relative to the rest of the measurements.

The average values of the magnitude, or absolute value of the deviations, $abs(\Delta SC_{wa})$, summarized in Table 2, Table 3, and Table 4, indicate that the lime stabilizer contents were determined most accurately using the WXRF method with average deviation magnitudes of 0.11%, and fly ash SCs were determined least accurately with average deviation magnitudes of 0.51%. Again, the latter observation is attributed to the two potential fly ash outliers near SC_a of 40%.

In Fig. 2 (b) the percent differences between SC_w and SC_a are plotted against the actual stabilizer contents, SC_a . This plot reveals that for lower SC_a values, the magnitude of deviations is much more important to the accuracy of the stabilizer content determination. For instance, if $abs(\Delta SC_{wa})$ is 0.5% and SC_a is 2%, the percent difference is 25%; however, for this same

deviation and SC_a of 15%, the percent difference near 3%. Thus, when trying to determine stabilizer contents at low percentages, the measurement deviations are much more important.

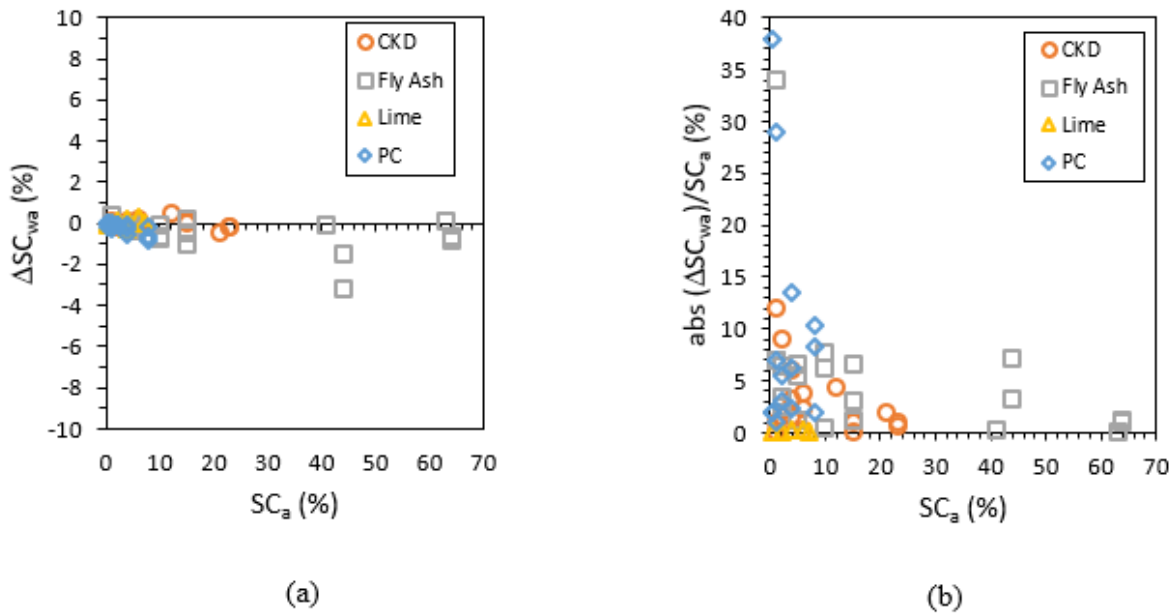


Figure 2. Influence of additive type on WXRF: a) the deviation between SC_w and SC_a versus SC_a ; b) $abs(\Delta SC_{wa})/SC_a$.

Table 2. Average influence of additive type on WXRF: Statistical analysis results.

Additive type	n	ΔSC_{wa} (%)	$abs(\Delta SC_{wa})$ (%)	$abs(\Delta SC_{wa})/SC_a$ (%)
All	63	-0.21	0.28	5.35
CKD	18	-0.02	0.15	2.82
Fly Ash	21	-0.45	0.51	5.35
Lime	10	0.02	0.11	4.40
PC	14	-0.23	0.23	9.29

Note: n equals the number of soil samples tested

Table 3. Standard Deviation of influence of additive type on WXRF: Statistical analysis results

Additive Type	n	ΔSC_{wa} (%)	$abs(\Delta SC_{wa})$ (%)	$abs(\Delta SC_{wa})/SC_a$ (%)
All	63	0.50	0.46	7.18
CKD	18	0.21	0.14	3.25
Fly Ash	21	0.76	0.72	7.10
Lime	10	0.16	0.12	3.91
PC	14	0.26	0.26	11.03

Note: n equals the number of soil samples tested

Table 4. Coefficient of deviation of influence of additive type on WXRF: Statistical analysis results

Additive Type	n	ΔSC_{wa} (%)	$abs(\Delta SC_{wa})$ (%)	$abs(\Delta SC_{wa})/SC_a$ (%)
All	63	-2.41	1.64	1.34
CKD	18	-8.49	0.97	1.15
Fly Ash	21	-1.67	1.40	1.33
Lime	10	10.85	1.07	0.89
PC	14	-1.13	1.12	1.19

Note: n equals the number of soil samples tested

3.2 Influence of Soil Type

Fig. 3 and Table 5, Table 6, and Table 7 show the influence of soil types on stabilizer content determined by the WXRF. In Fig. 3(a) and Table 3, it can be observed that the average deviation is slightly below zero for most of soil types and is greatest for SGB. The absolute values of the deviation $abs(\Delta SC_{wa})$, summarized in Table 3, indicates that the stabilizer contents of OHC soil were determined most accurately by the WXRF method with average deviation magnitudes of 0.09%, and stabilizer contents of SGB soil were determined least accurately with average deviation magnitudes of 0.38%.

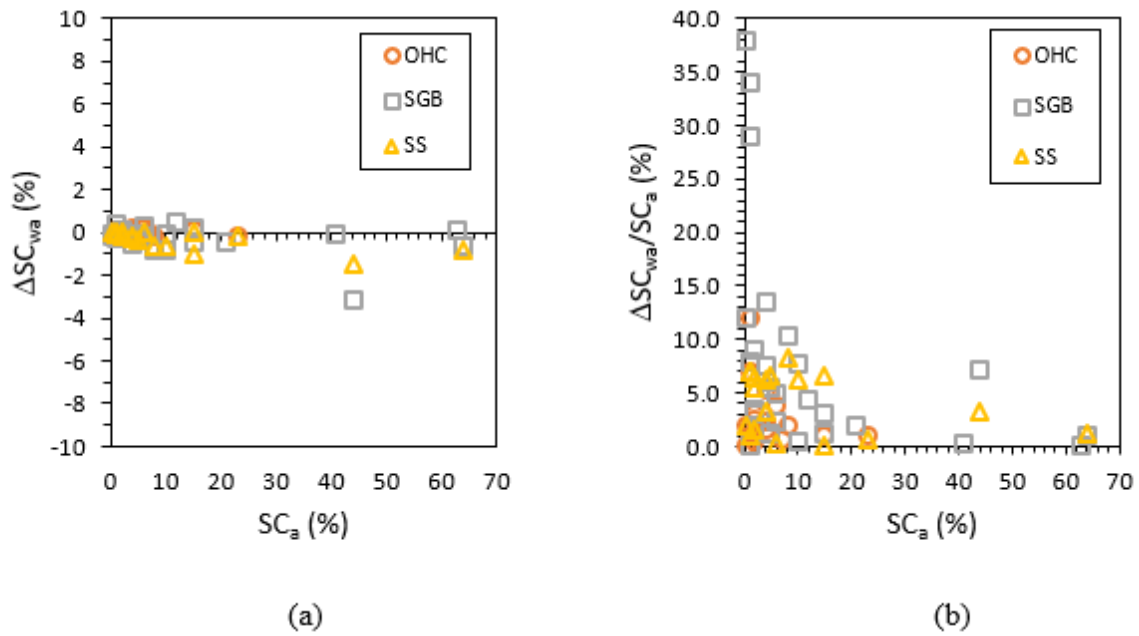


Figure 3. Influence of soil type on WXRF: a) the deviation between SC_w and SC_a versus SC_a ; b) $abs(\Delta SC_{wa})/SC_a$

Table 5. Average influence of soil type on WXRF: Statistical analysis results

Soil type	n	ΔSC_{wa} (%)	$abs(\Delta SC_{wa})$ (%)	$abs(\Delta SC_{wa})/SC_a$ (%)
All	63	-0.21	0.28	5.35
OHC	19	0.01	0.09	2.69
SGB	28	-0.27	0.38	7.97
SS	16	-0.33	0.33	4.09

Note: n equals the number of soil samples tested

Table 6. Standard deviation of influence of soil type on WXRF: Statistical analysis results

Soil type	n	ΔSC_{wa} (%)	$abs(\Delta SC_{wa})$ (%)	$abs(\Delta SC_{wa})/SC_a$ (%)
All	63	0.50	0.46	7.18
OHC	19	0.12	0.08	2.91
SGB	28	0.66	0.60	10.05
SS	16	0.42	0.42	2.84

Note: n equals the number of soil samples tested

Table 7. COV of influence of soil type on WXRF: Statistical analysis results

Soil type	n	ΔSC_{wa} (%)	$abs(\Delta SC_{wa})$ (%)	$abs(\Delta SC_{wa})/SC_a$ (%)
All	63	-2.41	1.64	1.34
OHC	19	12.30	0.91	1.08
SGB	28	-2.42	1.57	1.26
SS	16	-1.28	1.27	0.69

Note: n equals the number of soil samples tested

Chapter 4: PXRF Results

Fig. 4 (a) shows the PXRF data (SC_p) plotted against the WXRF data (SC_w), representing two different soil types and four different additive types. As shown, the intercept is far from zero at 1.047 and R^2 is 0.986, indicating that the PXRF method is not as accurate as the WXRF method in determining stabilizer content. Fig. 4 (b) illustrates the distribution of the SC_p deviation from the WXRF data (SC_w). While the PXRF results show overall larger deviation magnitudes than the WXRF data, we believe that with more refinement in sample preparation and calibration standards, the PXRF could more closely match the WXRF.

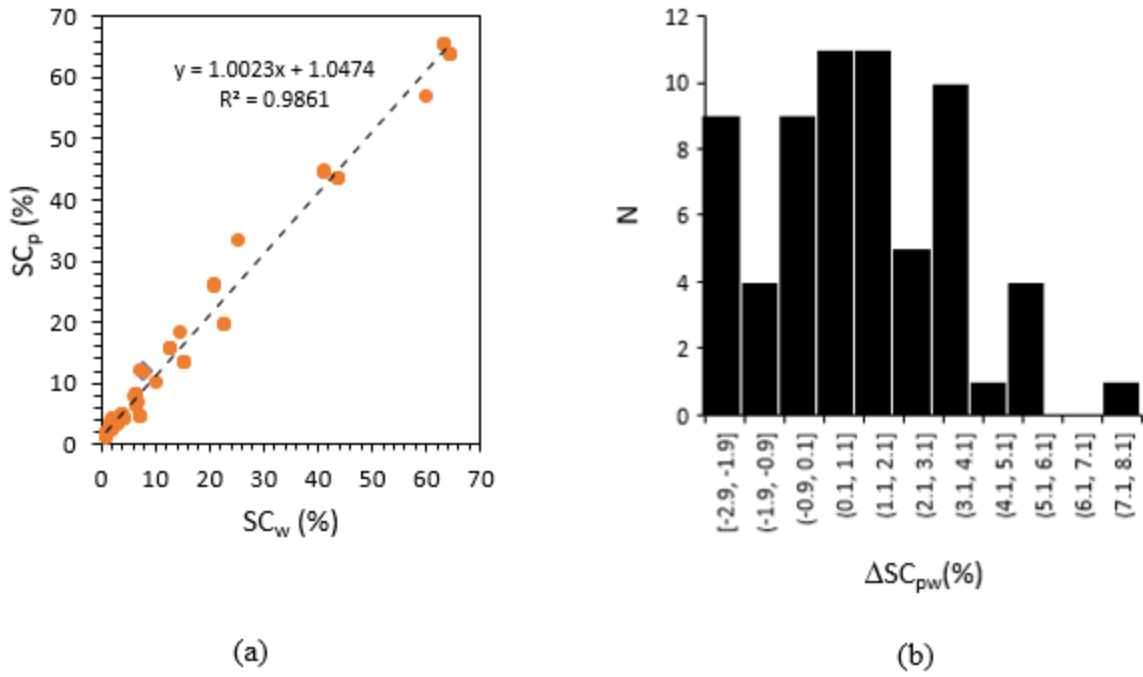


Figure 4. PXRF analysis: a) measured SC_p data versus SC_w data; b) the distribution of the deviation between SC_p and SC_w

4.1 Influence of Additive Type

The influence of additive type on stabilizer contents determined using the PXRF method is illustrated in Fig. 5 and in Table 8, Table 9, and Table 10, which summarizes the deviations (ΔSC_{pw}) between SC_p and SC_w. The average values of the magnitude (Table 4), or absolute value of the deviations $abs(\Delta SC_{pw})$ indicate that the lime stabilizer contents were determined most accurately by the WXRF method with average deviation magnitudes of 1.34%, and CKD SCs were determined least accurately with average deviation magnitudes of 3.13%. In Fig. 5 (b) the percent differences between SC_w and SC_a are plotted against the SC_w. This plot reveals that for lower SC_w values, the magnitude of deviations is much more important to the accuracy of the stabilizer content determination. As expected, this observation agrees with what shown by WRXF method, indicating that the measurement deviations are much more important when determining stabilizer contents at low percentages.

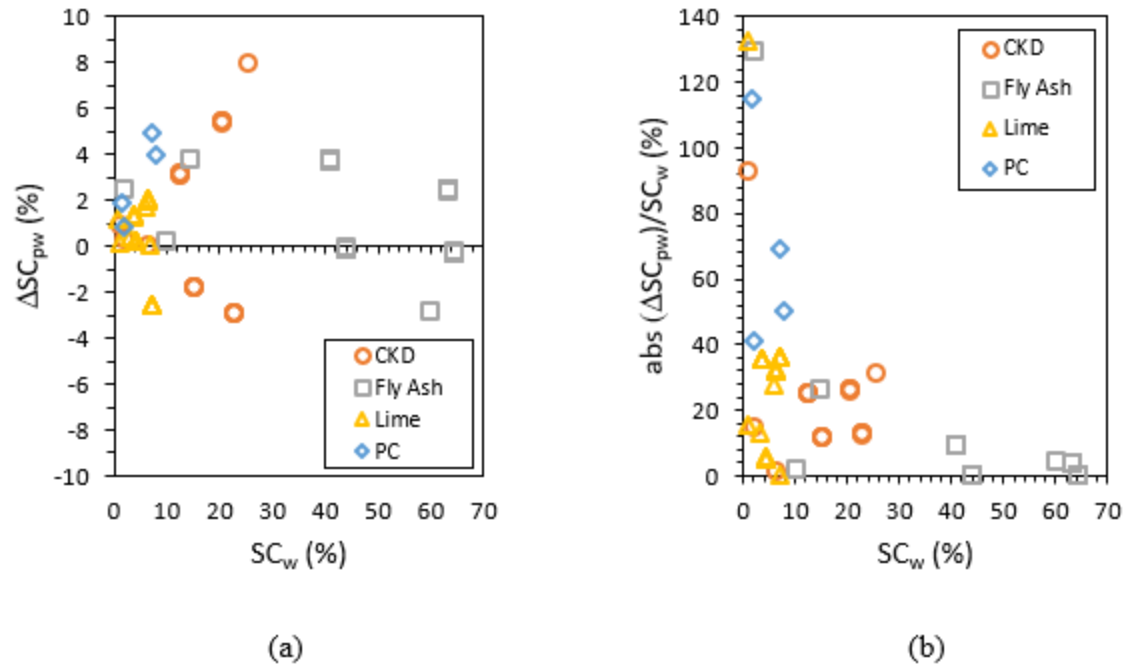


Figure 5. Influence of additive type on PXRF: a) the deviation between SC_p and SC_w versus SC_w ; b) $abs(\Delta SC_{pw})/SC_w$

Table 8. Average influence of additive type on PXRF: Statistical analysis results

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	47	1.10	2.13	24.12
CKD	13	1.25	3.13	22.30
Fly Ash	14	1.36	1.80	10.91
Lime	16	0.36	1.34	29.92
PC	4	2.90	2.90	68.80

Note: n equals the number of soils samples tested

Table 9. Standard deviation of influence of additive type on PXRF: Statistical analysis results

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	47	2.49	1.69	28.31
CKD	13	3.55	1.98	18.47
Fly Ash	14	1.97	1.56	28.58

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
Lime	16	1.61	0.92	27.04
PC	4	1.90	1.90	32.74

Note: n equals the number of soils samples tested

Table 10. COV of influence of additive type on PXRF: Statistical analysis results

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	47	2.27	0.80	1.17
CKD	13	2.84	0.63	0.83
Fly Ash	14	1.45	0.86	2.62
Lime	16	4.51	0.69	0.90
PC	4	0.65	0.65	0.48

Note: n equals the number of soils samples tested

4.2 Influence of Soil Type

Fig. 6 and Table 11, Table 12, and Table 13 present the influence of soil types on stabilizer content determined by the PXRF method. The silty sand is not shown in these figures because it exhibits quite different behavior in response to PXRF as shown in Table 14. The PXRF results for SS are presented separately in Fig. 7. As shown in Fig. 6(a), the influence of soil type on the accuracy of PXRF is consistent with what was observed for WXRF: the average deviation is below zero for most of soil types and is greatest for SGB. Table 5 presents the absolute values of the deviation, $abs(\Delta SC_{pw})$, indicating the stabilizer contents of OHC soil was determined most accurately by the PXRF method with average deviation magnitudes of 1.22%, and stabilizer contents of SGB soil were determined least accurately with average deviation magnitudes of 3.06%.

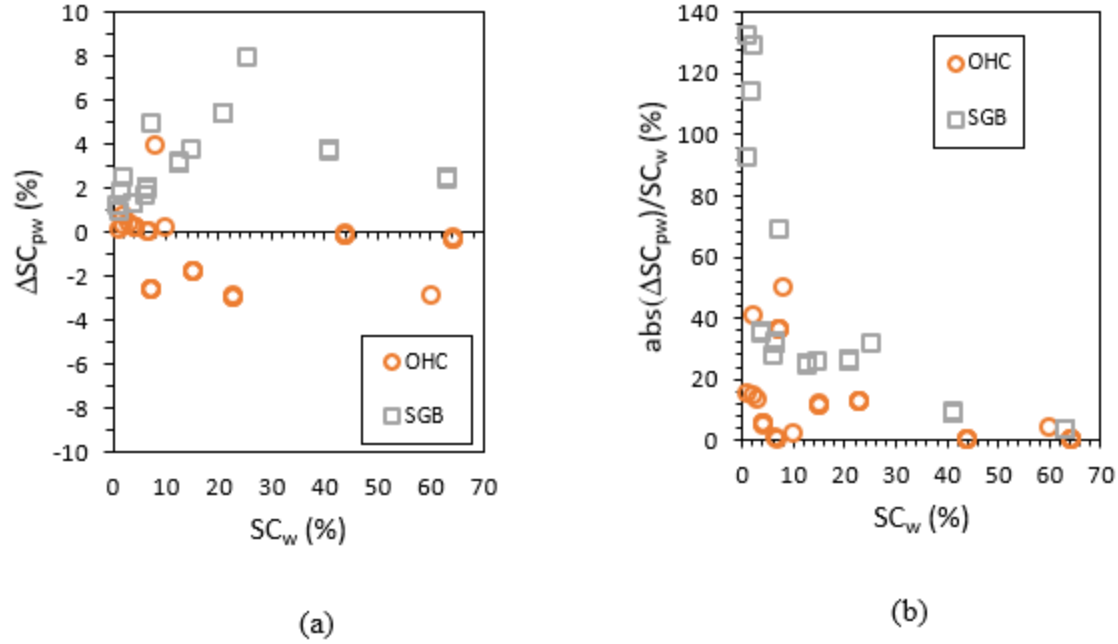


Figure 6. Influence of soil type on PXRF: a) the deviation between SC_p and SC_w versus SC_w; b) abs (ΔSC_{pw})/SC_w

Table 11. Average of influence of soil type on PXRF: Statistical analysis results

Soil type	n	ΔSC _{pw} (%)	abs(ΔSC _{pw}) (%)	abs(ΔSC _{pw})/SC _w (%)
All	47	1.10	2.13	24.12
OHC	25	-0.81	1.22	12.49
SGB	22	3.06	3.06	36.11

Note: n equals the number of soil samples tested

Table 12. Standard deviation of influence of soil type on PXRF: Statistical analysis results

Soil type	n	ΔSC _{pw} (%)	abs(ΔSC _{pw}) (%)	abs(ΔSC _{pw})/SC _w (%)
All	47	2.49	1.69	28.31
OHC	25	1.55	1.24	14.07
SGB	22	1.63	1.63	34.40

Note: n equals the number of soil samples tested

Table 13. COV of influence of soil type on PXRF: Statistical analysis results

Soil type	n	ΔSC _{pw} (%)	abs(ΔSC _{pw}) (%)	abs(ΔSC _{pw})/SC _w (%)
All	47	2.27	0.80	1.17
OHC	25	-1.92	1.01	1.13
SGB	22	0.53	0.53	0.95

As shown in Fig. 7, there were only seven samples analyzed using both PXRF and WXRF measurements and the PXRF method generally underperformed. The particle size may explain this behavior regarding PXRF accuracy because sand particles are mostly quartz, which have relatively larger diameters compared to clay minerals discussed in previous sections. However, the WXRF accuracy was excellent with the SS soil, which is likely due to the use of a fused disc, that is an amorphous solid for which particle size is irrelevant. Additional research is ongoing examining the importance of particle size, mineralogy, and crystal structure.

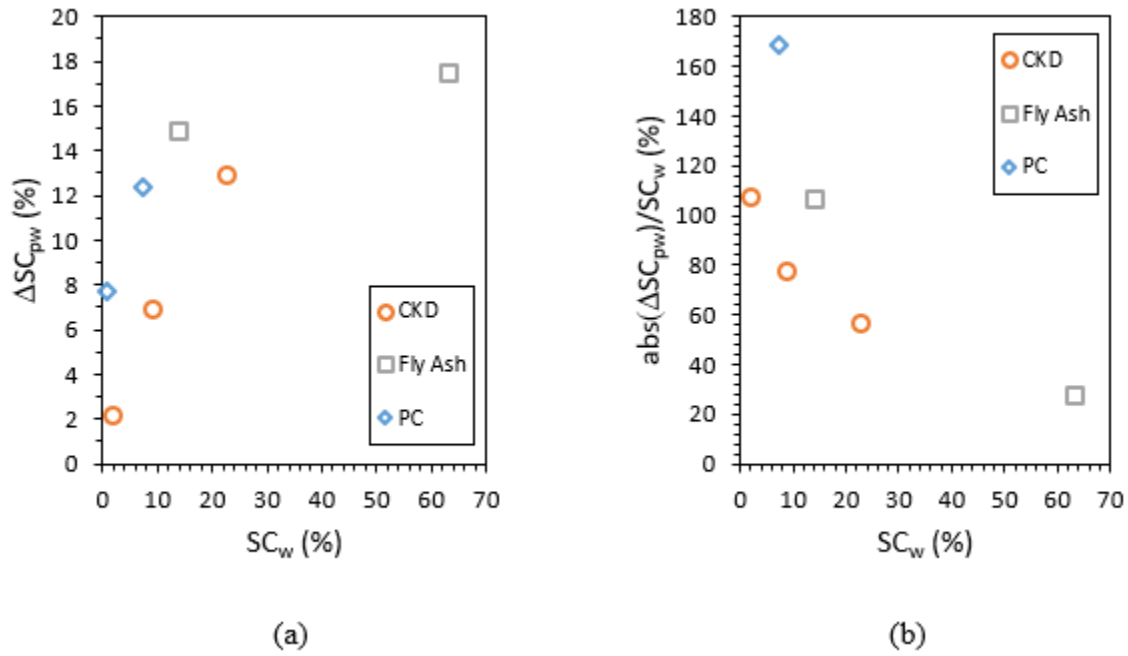


Figure 7. PXRF analysis for SS: a) the deviation between SC_p and SC_w versus SC_w; b) abs(ΔSC_{pw})/SC_w

Table 14. Statistical analysis results for SS

Statistical Test	Soil type	n	ΔSC _{pw} (%)	abs(ΔSC _{pw}) (%)	abs(ΔSC _{pw})/SC _w (%)
Average	SS	7	10.62	10.62	195.49
STDEV	SS		4.89	4.89	260.18
COV-STD	SS		0.46	0.46	1.33

Note: n equals the number of soils samples tested

4.3 Influence of Sample Preparation and Scanning Procedure

In order to better investigate the viability of the PXRF device for determining stabilizer content in treated soils, the influence of four independent variables associated with the test procedure are presented in the following sections, including: sample type (powder samples and pressed pellets), particle size (4.76 mm, 0.420 mm, 0.149 mm, and 0.074 mm), scan duration (60s, 75s, and 135s), and scan technique (standard or quartering). Note that silty sand is not included in this section and the following results are presented for SGB and OHC clays only.

4.3.1 Preparation using Pressed Pellet vs Powder

The sample types used in this research were pressed pellets and powder samples. There were not significant differences between these two different samples types as shown in Fig. 8 and Table 15, Table 16, and Table 17. 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, at least No. 40 sieve or finer, sample cups, and boPET film, whereas, pressed pellet samples require those items in addition to a hydraulic press, binding agent, laboratory scale, and sample cups. The pressed pellets also require approximately 15 minutes to create compared to 3 minutes for the loose powder samples. Therefore, in terms of field implementation, it is advantageous to use loose powder samples for PXRF analysis. Note that the recommended field procedure is still being evaluated.

Table 15. Average of influence of sample preparation on PXRF: Statistical analysis results

Sample type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	24	0.44	2.18	16.62
Powder	12	0.01	2.35	18.11
Pressed Pellet	12	0.88	2.02	15.13

Note: n equals the number of soils samples tested

Table 16. Standard deviation of influence of sample preparation on PXRF: Statistical analysis results

Sample type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	25	2.37	1.03	11.49
Powder	12	2.62	0.93	12.15
Pressed Pellet	12	2.24	1.18	11.65

Note: n equals the number of soils samples tested

Table 17. COV of influence of sample preparation on PXRF: Statistical analysis results

Sample type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	24	5.35	0.47	0.69
Powder	12	219.86	0.40	0.67
Pressed Pellet	12	2.56	0.58	0.77

Note: n equals the number of soils samples tested

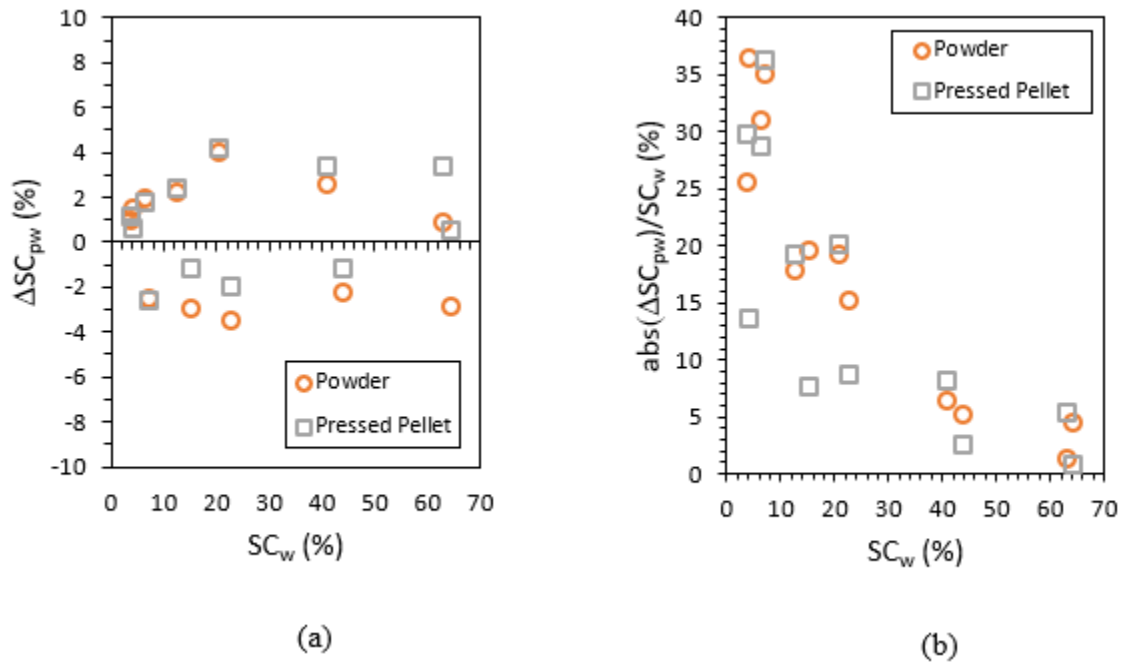


Figure 8. Influence of sample preparation on PXRF: a) the deviation between SC_p and SC_w versus SC_w ; b) $abs(\Delta SC_{pw})/SC_w$

4.3.2 Particle Size

Figs. 9 and Table 18, Table 19, and Table 20 show the impact of particle size on stabilizer contents determined using the PXRF method. The samples passing the #4 sieve have the highest deviation on average while the samples passing the rest of the sieves show variable results. In general, significant differences are not observed due to varying particle size between a #40 and a #200 sieve with OHC and SGB clays.

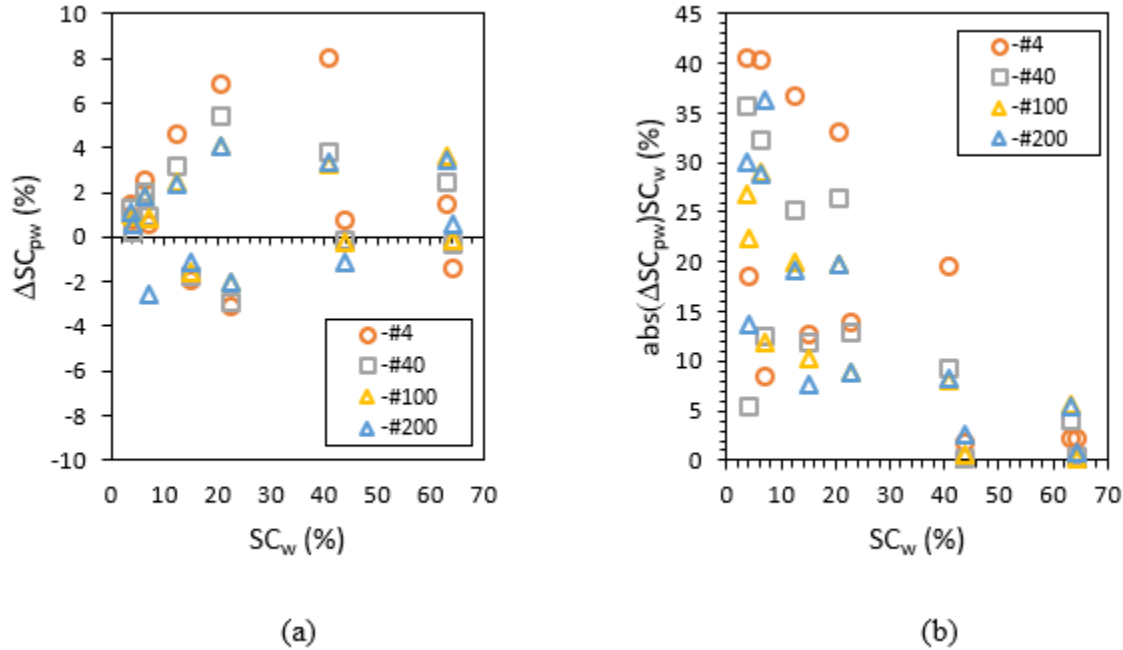


Figure 9. Influence of particle size on PXRF: a) the deviation between SC_p and SC_w versus SC_w ; b) $abs(\Delta SC_{pw})/SC_w$

While processing the clay samples over sieves ranging from 0.425 mm (#40) to 0.075 mm (#200) seemed to have a relatively minor effect on the accuracy of the measurements, it is clear from the preceding discussion of soil types (Section 4.2) that the sandy soil (SS) milled to pass a #40 sieve resulted in much less accurate measurements using the PXRF device. It is believed that the relatively large sand particles, composed primarily of crystalline quartz, and up to 0.425 mm in size, are the primary cause of the observed inaccuracy with the SS soil. It is possible that the x-ray scattering through the small PXRF sample volume is more random and less repeatable when a significant number of randomly oriented larger crystalline particles are present. For comparison, the clay minerals in OHC and SGB have crystal sizes around 0.002 mm or less. It is

also important to note that for the fused discs, where particle size is irrelevant, the accuracy of stabilizer content measurements on SS samples was on par with that of OHC and SGB samples.

Table 18. Average of influence of particle size on PXRF: Statistical analysis results

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	48	1.24	2.17	15.64
-#4	12	1.72	2.80	19.16
-#40	12	1.19	2.04	14.67
-#100	12	1.18	1.83	13.62
-#200	12	0.87	2.01	15.10

Note: n equals the number of soil samples tested

Table 19. Standard deviation of influence of particle size on PXRF: Statistical analysis results

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	48	2.45	1.68	11.97
-#4	12	3.36	2.45	14.95
-#40	12	2.37	1.61	12.27
-#100	12	1.96	1.30	9.78
-#200	12	2.23	1.17	11.65

Note: n equals the number of soil samples tested

Table 20. COV of influence of particle size on PXRF: Statistical analysis results

Additive type	n	ΔSC_{pw} (%)	$abs(\Delta SC_{pw})$ (%)	$abs(\Delta SC_{pw})/SC_w$ (%)
All	48	1.97	0.77	0.77
-#4	12	1.95	0.88	0.78
-#40	12	2.00	0.79	0.84
-#100	12	1.66	0.71	0.72
-#200	12	2.56	0.58	0.77

Note: n equals the number of soil samples tested

4.3.3 Scan Type and Scan Duration

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. The accuracy was only minorly affected by scan types. From an efficiency standpoint, a standard scanning technique is more appropriate because it requires four times fewer scans per sample than the quartering technique.

Scan durations longer than 60 seconds (30s-30s) do not increase the accuracy and precision of the device measurements. This observation was expected because the CaO element measured by PXRF has a specific atomic number and uses a known amount of energy to hold the electrons in their orbits. If this element is exposed to X-ray radiation with energies equal to or just greater than the energy holding the electrons in their orbits, the X-ray radiation most likely can knock bound electrons out of their orbits and displace them (Moore and Jr, 1989). In this study, the magnitude of the X-ray radiation energy remains constant for the different scan durations. Therefore, longer scan durations do not change the accuracy of this measurement because the samples are exposed to the same amount of energy.

Chapter 5: Investigation of Various PXRF Libraries in Detecting Stabilizer Content

5.1 Laboratory Mixed Samples

Calibration standards of known elemental compositions were created in order to verify PXRF results. These reference samples were mixed using four base soils and four chemical stabilizers. The base soils included three bentonites and one kaolinite: Super Gel-X Bentonite (SGB), Fisher Bentonite B235-500 (F), Fossil Power Bentonite (FPB) and the Kaolinite Old Hickory Clay (OHC). The four chemical stabilizers used include Fly Ash (FA), Cement Kiln Dust (CKD), Portland Cement (PC) and Lime. The mix design matrix for Bentonite samples can be found in Tables 21-24 and the mix design matrix for Kaolinite samples is presented in Tables 25-28.

Table 21. Bentonite and Class C Fly Ash mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	2.3	1.6	1.3
2	2.5	1.8	2.2

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
3	2.8	2.0	3.5
5	3.2	2.3	5.4
10	4.5	3.2	10.6
15	5.7	4.0	15.6
20	6.8	4.9	20.5

Table 22. Bentonite and Cement Kiln Dust mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	2.4	1.7	1.1
2	2.9	2.0	2.1
3	4.1	2.9	4.9
5	5.9	4.2	9.3
10	6.1	4.3	9.6
15	8.1	5.8	14.3
20	10.3	7.4	19.5

Table 23. Bentonite and Portland Cement mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	1.8*	1.3	1.0
2	2.4*	1.7	1.9
3	3.8	2.7	4.1
5	4.8	3.4	5.7
10	7.7	5.5	10.3
15	--	--	--
20	13.0	9.3	18.8

Note: * Indicates bentonite type F used

Table 24. Bentonite and Lime mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1.9*	1.4	0.9	1.9*
3.0 [†]	2.2	2.3	3.0 [†]
3.6 [†]	2.5	3.1	3.6 [†]
4.8 [†]	3.5	4.9	4.8 [†]
8.1 [†]	5.8	9.5	8.1 [†]
--	--	--	--
14.3 [†]	10.2	18.3	14.3 [†]

Note: * Indicates bentonite type F used

[†] Indicates bentonite type FPB used

Table 25. Kaolinite and Class C Fly Ash mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	0.4	0.3	1.1
2	0.7	0.5	2.1
3	0.9	0.7	3.1
5	1.5	1.0	5.1
10	2.9	2.0	10.6
15	4.1	2.9	15.5
20	5.5	3.9	20.9

Table 26. Kaolinite and Cement Kiln Dust mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	0.6	0.4	1.1
2	1.0	0.7	2.0
3	1.4	1.0	2.9
5	2.4	1.7	5.1
10	4.7	3.3	10.2
15	6.9	4.9	15.2
20	9.0	6.4	19.9

Table 27. Kaolinite and Portland Cement mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	0.7	0.5	0.9
2	1.4	1.0	2.0
3	2.0	1.4	2.9
5	3.1	2.2	4.7
10	6.3	4.5	9.7
15	--	--	--
20	11.9	8.5	18.5

Table 28. Kaolinite and Lime mix design matrix

SC (%)	WRA CaO (%)	WRA Ca (%)	WRA SC (%)
1	0.8	0.6	1.0
2	1.5	1.1	2.0
3	2.2	1.6	2.9
5	3.6	2.6	4.9
10	7.0	5.0	9.6
15	--	--	--
20	13.9	9.9	19.1

Whole Rock Analysis (WXRF) was used to verify the laboratory-manufactured samples reached the target mix design. Since WXRF has been shown to produce reliable results (Cerato and Miller, 2013; Bourke and Ross, 2015), the manufactured samples can be used as reference standards to verify and calibrate all PXRF measurements. PXRF calibration libraries used include Limestone – Cement, GeoExplore, and GeoMine. Both WXRF and Limestone – Cement directly measure calcium oxide (CaO), whereas both the GeoExplore and GeoMine calibrations measure calcium (Ca). Therefore, Limestone results can be directly compared to WXRF, but GeoExplore and GeoMine results must be converted according to the factors presented in Table 29 before comparing to WXRF values.

Whole rock analysis was used to confirm the target mix designs and also serves as the reference standard for all portable handheld (PXRF) measurements. While the PXRF measures calcium or calcium oxide directly, the percent of stabilizer content (SC) is the desired parameter. This SC value can be calculated using Equation 1:

In order to accurately measure the stabilizer content, the calcium (or calcium oxide) measurements must be collected from three samples: (1) the untreated soil, (2) the stabilized soil, and (3) the chemical additive (stabilizer). It has been shown that these values can be reliably measured using various libraries, both with and without calibration coefficients. Once these measurements were collected, the SC of the mixed standards was determined.

Table 29. Conversion between CaO and Ca and Ca to CaO.

Conversion	Formula
CaO to Ca	$\text{CaO} * 0.7147 = \text{Ca}$
Ca to CaO	$\text{Ca} * 1.3992 = \text{CaO}$

Figure 10 and Figure 11 reveal that the PXRF measurements of Ca and CaO in the stabilized soils are reliable, i.e., show minimal variance from the 1:1 line. All three uncalibrated standards read the amount of Calcium or Calcium oxide over the full range accurately, with the Limestone-Cement calibration showing bias toward the PXRF measurements in the upper ranges. Due to the accuracy of the PXRF to measure known elemental values of the soil standards, it shows promise as a tool to measure the stabilizer content of subgrade soils. However, it is necessary to determine the Calcium content of the chemical stabilizer first in order to perform these measurements.

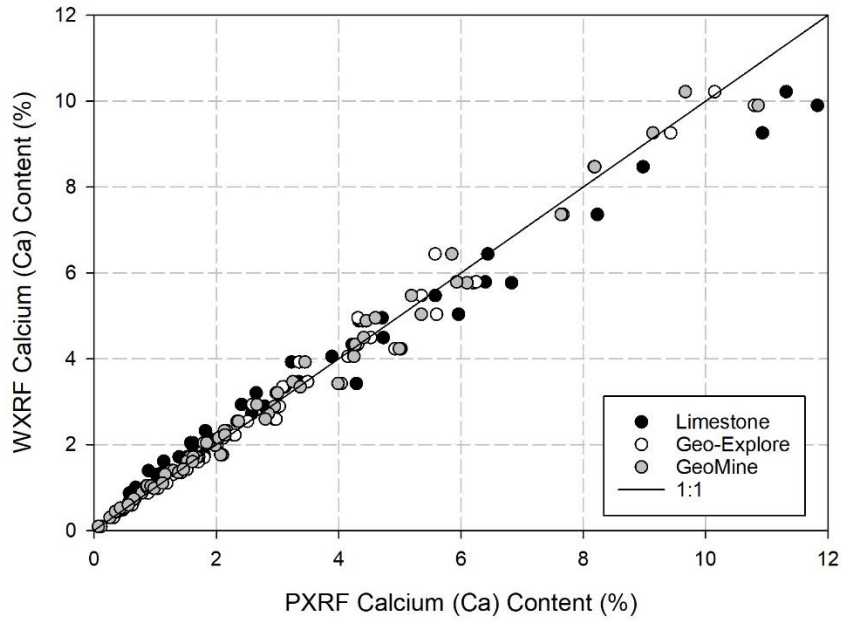


Figure 10. Comparison between PXRF and WXRF measurements of Calcium (Ca).

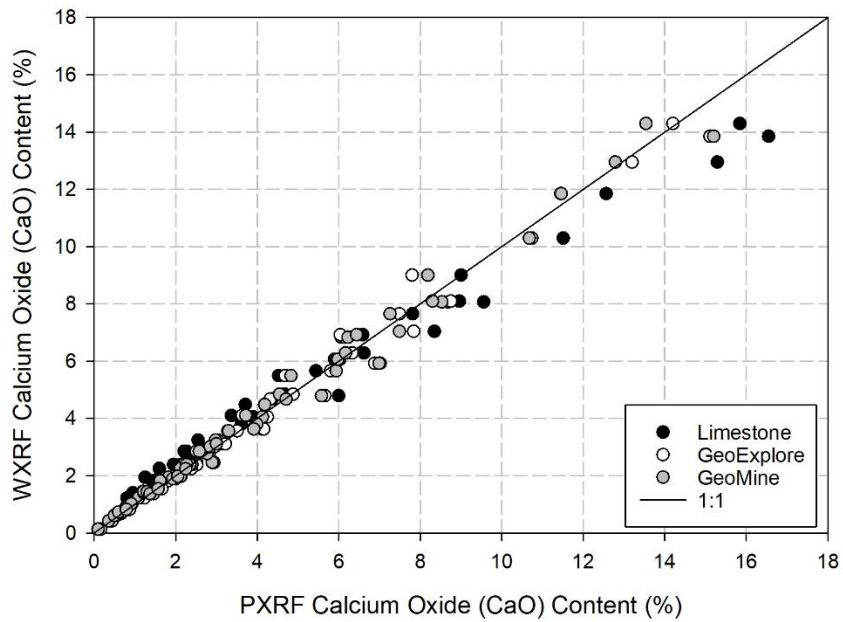


Figure 11. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO).

As shown in Figure 12, the SC of the stabilizers varied widely from the 1:1 line using the uncalibrated libraries. Higher accuracy is associated with smaller variance from the 1:1 line, as the coefficient of determination (R^2) values will approach 1 for specimens with lower variance.

Therefore, in order to determine the stabilizer content of a soil, it is necessary to calibrate with pure stabilizers first. It is unclear why the three existing libraries (e.g., Limestone-Cement, GeoExplore, GeoMine), measure the lower ranges of calcium content in the stabilized soils well without using a slope correction, but do not accurately measure the calcium content of Portland Cement, Cement Kiln Dust, Fly Ash, or Limestone in the higher ranges.

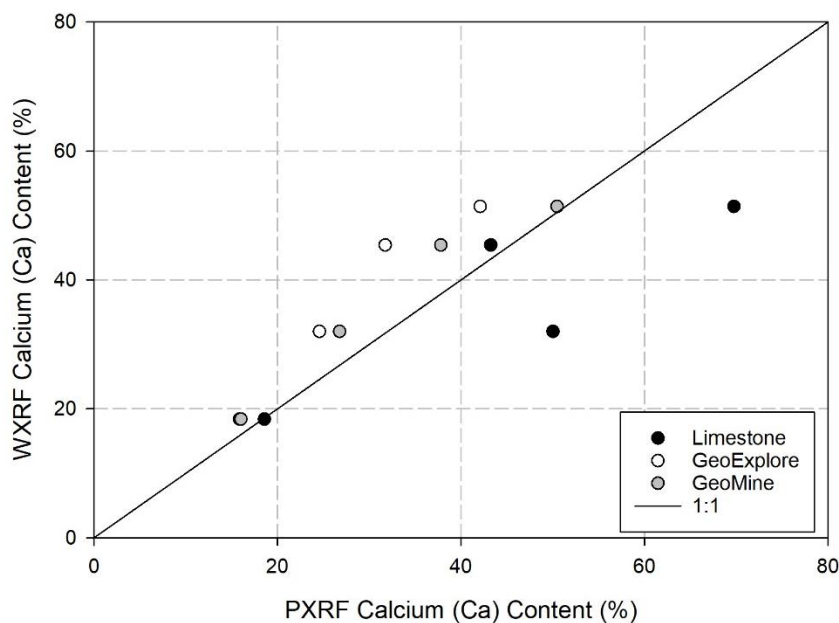


Figure 12. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO) of the chemical stabilizers.

The calibration curves for both GeoExplore and GeoMine appear to be bi-linear. Therefore, the lime series are isolated from the total data and FA, CKD, and PC are plotted together (Figure 13). Only the slope and offsets from the PC, CKD, and FA series are used for this calibration. However, due to the bilinear nature of these calibrations, the calibration coefficients are not used for calcium contents greater than 45%.

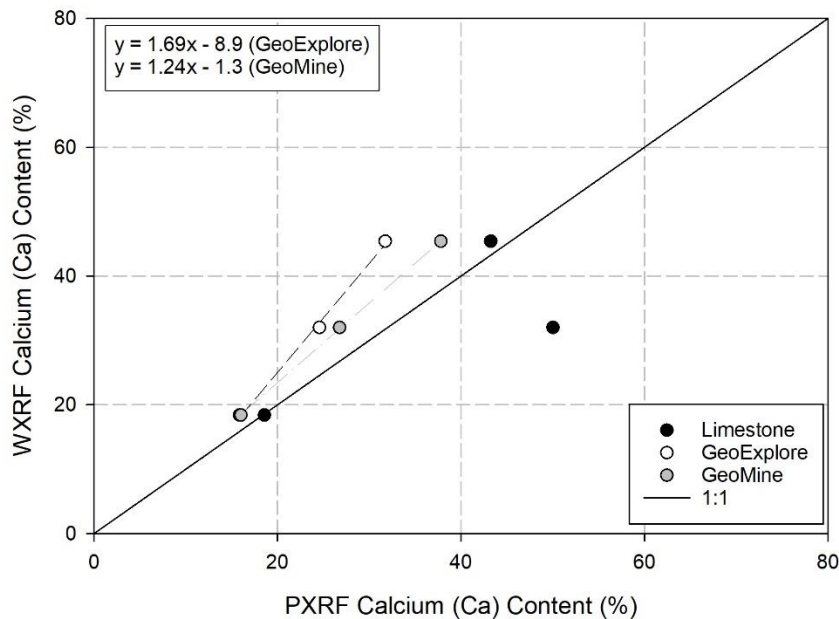


Figure 13. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO) of the chemical stabilizers with less than 45% calcium contents.

The Limestone – Cement Library shows no real linear trend between Portland Cement, Fly Ash and Cement Kiln Dust; however, both GeoExplore and GeoMine do appear linear. After applying the slope coefficients to both the GeoExplore and GeoMine libraries for the Portland Cement, Cement Kiln Dust and Fly Ash stabilizers, PXRF measurements appear to more accurately measure the calcium content of the stabilizers. Additionally, the calcium content of the lime-stabilized series is measured accurately using the GeoMine library without a calibration coefficient. Therefore, it is necessary to apply a coefficient when using PXRF to detect chemical stabilizers only on projects using Portland Cement, CKD or FA, while the standard libraries without a coefficient are sufficient to measure a lime-based chemical stabilizer. Therefore, the following recommendations can be made:

- (1) When measuring the calcium element of PC, CKD, and FA stabilizers, the GeoMine library with 1.24 slope calibration coefficient should be used
- (2) When measuring the calcium content of lime stabilizers, the GeoMine library should be used with no calibration coefficients
- (3) Send all chemical stabilizers out for Whole Rock Analysis to verify the GeoMine PXRF calcium oxide measurements.

This will ensure that the calcium content measured is accurate and can then be used in the stabilizer content calculation on a stabilized subgrade soil.

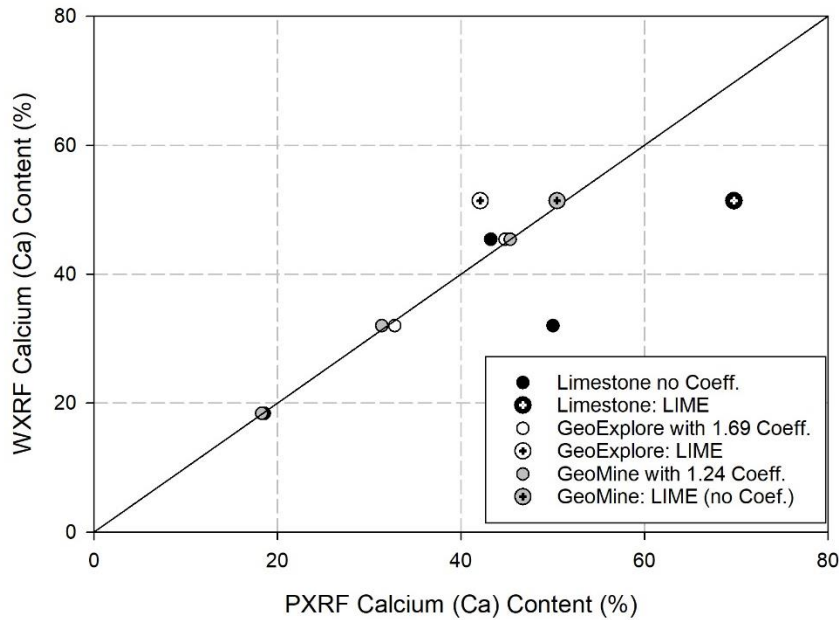


Figure 14. Comparison between PXRF and WXRF measurements of Calcium Oxide (CaO) of the chemical stabilizers with slope coefficients to both the GeoExplore and GeoMine libraries for the Portland Cement, Cement Kiln Dust and Fly Ash stabilizers.

Figure 15 shows the calculated SC of all mixed samples, including PC, Lime, FA, and CKD stabilized soils, without calibration coefficients. From this figured, it can be seen that below 7% SC, all three libraries are fairly accurate in measuring the SC. However, for SC greater than 7%, only the GeoExplore and GeoMine calibrations follow the 1:1 line, while the Limestone – Cement calibration shows greater variation. While the PXRF results presented were obtained using calibration libraries without calibration coefficients, the calcium content of the stabilizers themselves for CKD, FA, and PC were determined using unique coefficients: GeoExplore: 1.69, GeoMine: 1.24, Limestone: no coefficients. These measured values were used to calculate the stabilizer content of the stabilized soils. No calibration coefficients were used for lime stabilizers in any of the three libraries.

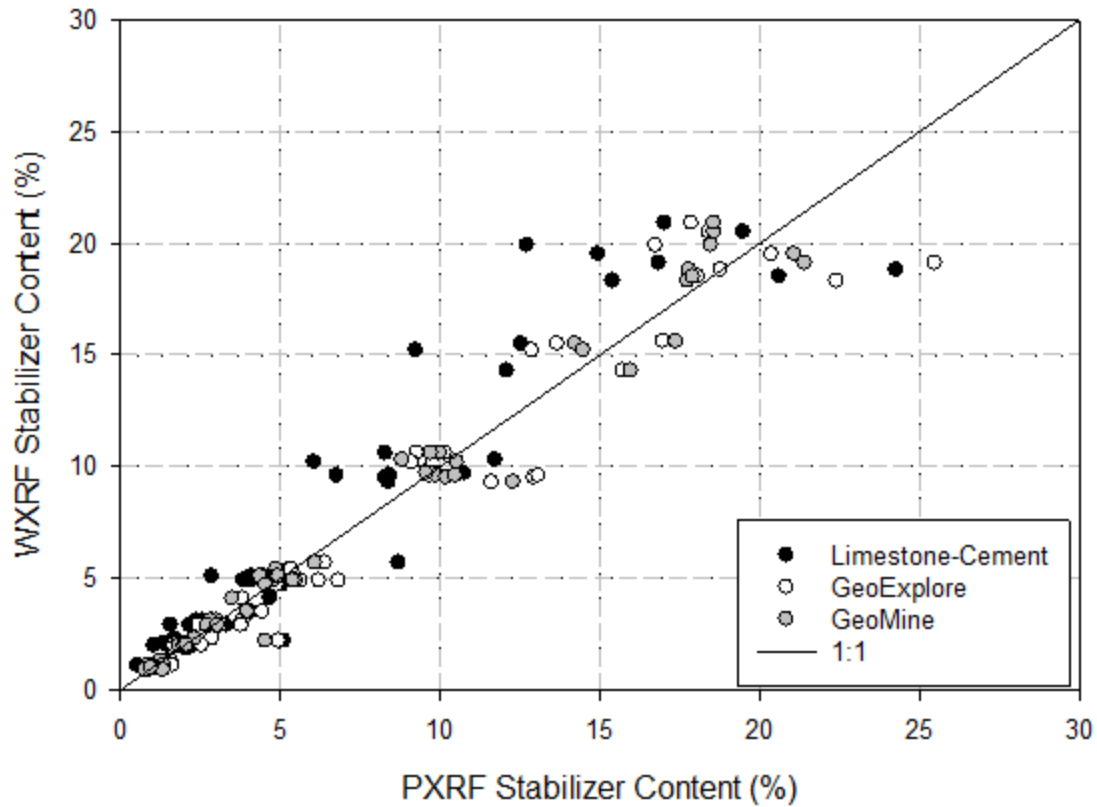


Figure 15. Calculated SC of all mixed samples, including PC, Lime, FA, and CKD stabilized soils, without calibration coefficients.

5.2 Field Samples

Once the ability of the GeoMine and GeoExplore libraries to accurately measure the CaO content of both untreated and stabilized soils were verified, all samples were measured using PXRF.

Table 30 and Figure 16 show the field sites sampled for this research project.

Table 30. The Field Sites, Locations, and Design Percentage.

Field sites	Location	Stabilizer detail
Site 1	Hwy 59, Wayne, 73095	3% Portland Cement (PC)
Site 2	Hwy 53, Springer, 73458	3% Lime (Pellet Quicklime)
Site 3	State Highway 29, Marlow, 73055	3% Portland Cement (PC)
Site 4	534 Highway 77S, Ardmore, 73402	3% Portland Cement (PC)
Site 5	SE 89th Street, Shields Boulevard, 73149	3% Lime (pellet quicklime)
Site 6	4651 N. Harrison Ave, Shawnee, 74804	10% Cement Kiln Dust (CKD)

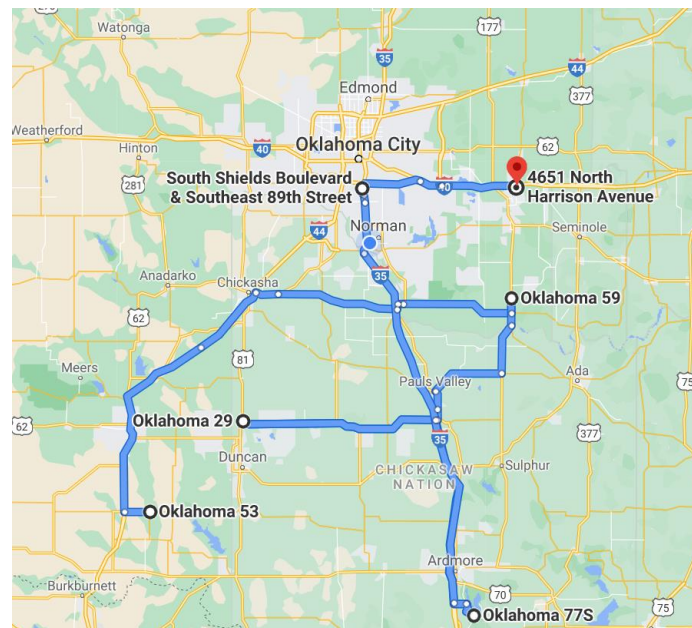


Figure 16. Map of Field Testing Locations

The samples from these sites were tested to assess dosing and mixing adequacy according to the procedures and protocols determined through this research project. SC of the stabilized soils were compared to the design percentages (Tables 31 and 32). Field samples were prepared according to Standard Sampling and Testing Procedure and Contractor Specifications (Chapter 6). Figure 17 shows the variation of SC determined using PXRF of a 10-foot square stabilization project at Site 6. The contour highlights the homogeneity of the field mixing procedure.

Table 31. Field site stabilizer content values using GeoMine (Sites 1 – 5)

Site	Stabilizer	Design SC (%)	Soil ID	GeoMine SC (%)
Site 1	CKD	10	Shawnee #1: LP #1	29.0
Site 1	CKD	10	Shawnee #2: LP #2	20.2
Site 1	CKD	10	Shawnee #3: PP #1	27.4
Site 1	CKD	10	Shawnee #4: PP #3	21.1
Site 1	CKD	10	Shawnee #5: E. Corner of Bldg.	16.5
Site 2	PC	3	SH 29: CL	8.5
Site 3	PC	3	Noble Gray: CL	26.0
Site 4	Lime	3	HW 53: 1	6.1
Site 4	Lime	3	HW 53: 2	4.7
Site 4	Lime	3	HW 53: 3	14.3
Site 4	Lime	3	HW 53: 4	6.1
Site 4	Lime	3	HW 53: 5	2.3
Site 4	Lime	3	HW 53: 6	31.9
Site 4	Lime	3	HW 53: 7	7.5
Site 4	Lime	3	HW 53: 8	3.7
Site 4	Lime	3	HW 53: 9	29.6
Site 5	Lime	3	Stanley Rother: 1	7.5
Site 5	Lime	3	Stanley Rother: 2	4.4
Site 5	Lime	3	Stanley Rother: 3	11.1
Site 5	Lime	3	Stanley Rother: 4	33.9
Site 5	Lime	3	Stanley Rother: 5	3.1
Site 5	Lime	3	Stanley Rother: 6	5.9
Site 5	Lime	3	Stanley Rother: 7	7.9
Site 5	Lime	3	Stanley Rother: 8	26.6
Site 5	Lime	3	Stanley Rother: 9	5.7
Site 5	Lime	3	Stanley Rother: 10	7.0
Site 5	Lime	3	Stanley Rother: 11	11.3
Site 5	Lime	3	Stanley Rother: 12	5.2
Site 5	Lime	3	Stanley Rother: 13	18.6
Site 5	Lime	3	Stanley Rother: 14	12.5
Site 5	Lime	3	Stanley Rother: 15	11.9
Site 5	Lime	3	Stanley Rother: 16	6.0
Site 5	Lime	3	Stanley Rother: 17	18.2
Site 5	Lime	3	Stanley Rother: 18	9.1
Site 5	Lime	3	Stanley Rother: 19	12.7
Site 5	Lime	3	Stanley Rother: 20	6.3

Table 32. Field site stabilizer content values using GeoMine (Site 6)

Site	Stabilizer	SC (%)	Soil ID	GeoMine SC (%)
Site 6	PC	3	Wayne Payne 0-3" N	3.5
Site 6	PC	3	Wayne Payne: 3-6" N	4.8
Site 6	PC	3	Wayne Payne: 6-9" N	4.1
Site 6	PC	3	Wayne Payne: 9-12" N	0.2
Site 6	PC	3	Wayne Payne: 0-3" NE	1.3
Site 6	PC	3	Wayne Payne: 3-6" NE	0.5
Site 6	PC	3	Wayne Payne: 6-9" NE	1.0
Site 6	PC	3	Wayne Payne: 9-12" NE	0.0
Site 6	PC	3	Wayne Payne: 0-3" SW	12.5
Site 6	PC	3	Wayne Payne: 3-6" SW	12.3
Site 6	PC	3	Wayne Payne: 6-9" SW	12.0
Site 6	PC	3	Wayne Payne: 9-11" SW	15.4
Site 6	PC	3	Wayne Payne: 0-3" CL	5.5
Site 6	PC	3	Wayne Payne: 3-6" CL	5.2
Site 6	PC	3	Wayne Payne: 6-9" CL	4.6
Site 6	PC	3	Wayne Payne: 9-12" CL	0.4
Site 6	PC	3	Wayne Payne: 0-3" W	6.8
Site 6	PC	3	Wayne Payne: 3-6" W	8.7
Site 6	PC	3	Wayne Payne: 6-9" W	9.3
Site 6	PC	3	Wayne Payne: 9-11" W	3.4
Site 6	PC	3	Wayne Payne: 0-3" NW	7.7
Site 6	PC	3	Wayne Payne: 3-6" NW	8.1
Site 6	PC	3	Wayne Payne: 6-9" NW	8.7
Site 6	PC	3	Wayne Payne: 9-11" NW	6.0
Site 6	PC	3	Wayne Payne: 0-3" E	0.3
Site 6	PC	3	Wayne Payne: 3-6" E	2.0
Site 6	PC	3	Wayne Payne: 6-9" E	2.3
Site 6	PC	3	Wayne Payne: 9-12" E	0.0
Site 6	PC	3	Wayne Payne: 0-3" S	4.6
Site 6	PC	3	Wayne Payne: 3-6" S	2.9
Site 6	PC	3	Wayne Payne: 6-9" S	3.3
Site 6	PC	3	Wayne Payne: 9-12" S	0.7
Site 6	PC	3	Wayne Payne: 0-3" SE	1.9
Site 6	PC	3	Wayne Payne: 3-6" SE	1.5
Site 6	PC	3	Wayne Payne: 6-9" SE	3.3
Site 6	PC	3	Wayne Payne: 9-12" SE	1.2

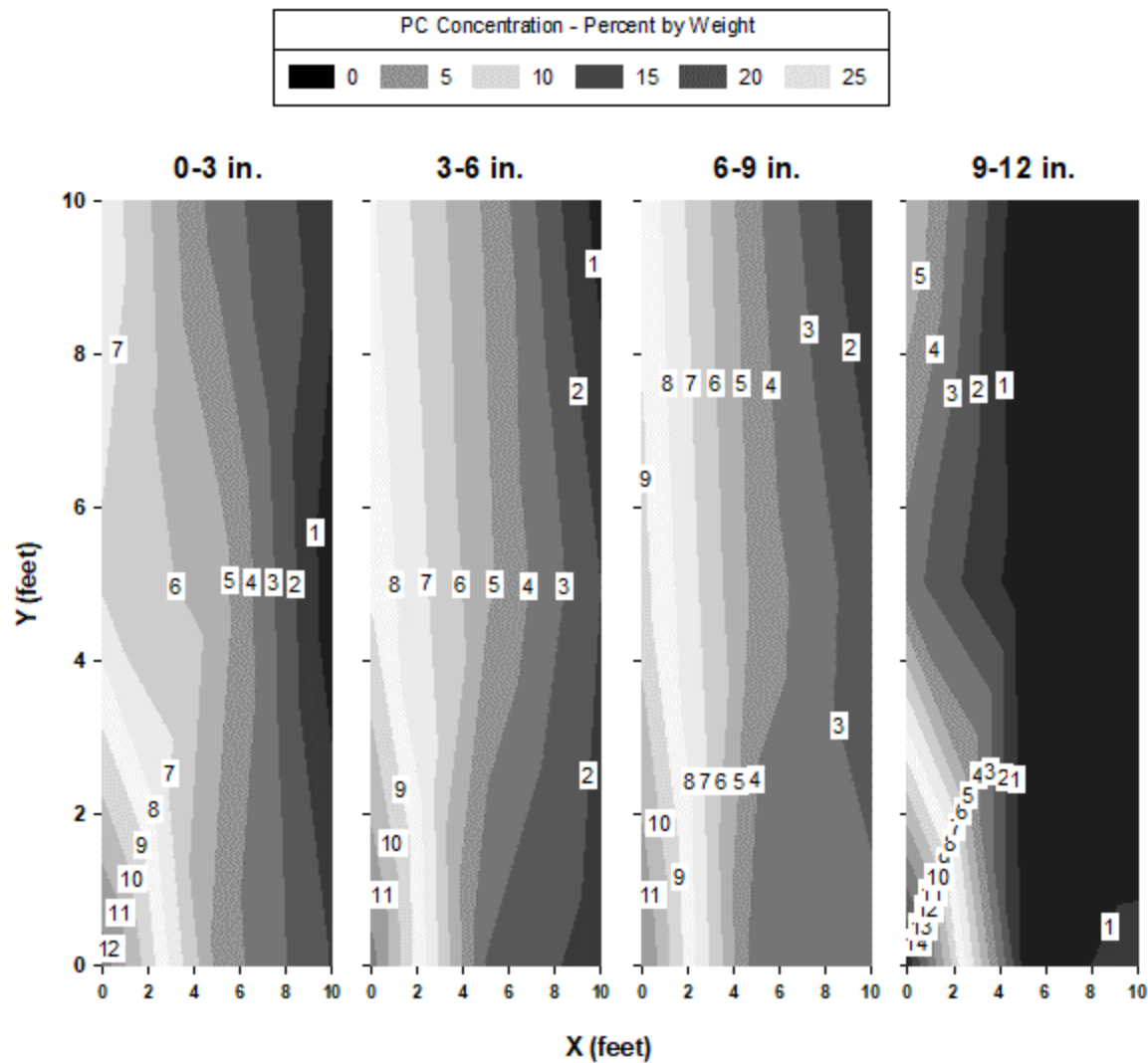


Figure 17. Variation of PC content in 10 ft x10 ft test section of Wayne Payne site determined by PXRF measurement. (Design PC 3%).

Chapter 6: Standard Sampling and Testing Procedure and Contractor Specifications

6.1 Sampling and Testing Procedure

The following specifications must be met if testing using PXRF:

- Site must be sampled prior to stabilization to establish a pre-stabilized Calcium value, i.e., virgin soil.
- Chemical Stabilizer must be collected to establish calcium content in the stabilizer.

- Stabilized soil must be sampled randomly on site after compaction.
- These three ~100 gram samples (untreated soil, chemical stabilizer and stabilized soil) should be dried and pulverized to pass a number #40 sieve. (Ideally a No. 200 sieve)

Samples must be placed in sample cup in the following procedure:

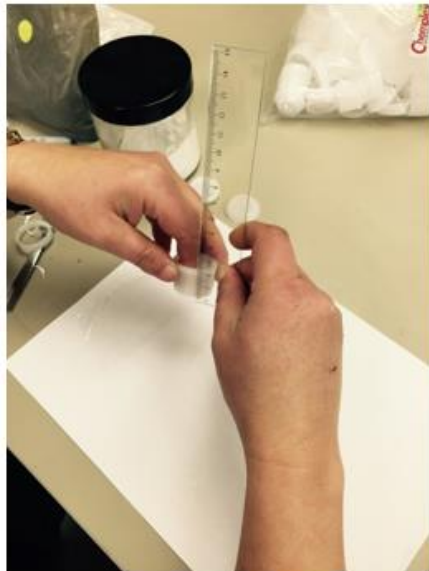
1. Ensure that the proper tools are available. Necessary tools include:
 - a. Double open-sided 31mm diameter sample cups with lids (Chemplex part # 1330)
 - b. 4-micron prolene or ultralene film
 - c. Scoop
 - d. Cotton balls
 - e. Round paper cutouts to fit inner diameter of sample cup (24mm)
 - f. Tapered or 24mm max diameter dowel to press powder in the cup
 - g. Paper towels or other cloth to wipe down tools and area
 - h. Ruler with millimeter divisions
 - i. Sharpie
2. Place 4-micron prolene film on the opposite end of the sample cup from the lid and hold in place by securing the cap ring (Figure 18a). Ensure there are no tears in the film after attaching the cap ring. Also verify that the cap is fully in place, creating a flat surface (Figure 18b).
3. With the ruler, measure from the film end. Delineate the appropriate height of the sample using the Sharpie (Figure 18c and 18d). For data collection samples, sample height is 1.5cm. For check samples desired height is 1cm. Other types of samples may have other requirements.



(a)



(b)



(c)



(d)

Figure 18. Specimen preparation: a) Place cap ring over foil; b) Ensure cap ring is fully on; c) Measure from film end; and d) Mark with pen.

4. Place the sample cup film-side down and scoop the sample powder into the cup, filling to the sample height line, marked using Sharpie. Settle the loose powder in the sample by gently tapping the sample cup.

5. Use the dowel to push the powder down, compacting it to eliminate air gaps between particles (Figure 19a). Using the paper separators from between the Ultralene sheets to cover the dowel will make it easier to clean the dowel between samples. The powder may try to push up the sides of the cup or spray out around the edges, especially if the density is very low. If powder escapes from the sides of the cup, shake/tap the cup or use the scoop to move the powder back to the middle. Gloves can be worn as a precaution if the material should not come into contact with the skin.
6. If the pressed powder is below the Sharpie line, scoop more powder into the cup, and proceed to step 5, repeating the process until the pressed powder comes approximately to the Sharpie line.
7. Place the precut paper round into the sample cup on top of the powder (Figure 19b). If using a piece larger than the diameter of the cup, use the scoop to press the edges down to ensure that the powder will not escape the sides.



(a)



(b)

Figure 19. Specimen preparation: a) Press the powder with a dowel; b) Place paper circle on top of sample.

8. Place the cotton ball on top of the paper and press it into the cup until it fills all remaining space in the cup (Figures 20a and 20b). If the cup is too full to use a whole cotton ball, rip off part of the cotton until it packs down into the remaining space.



(a)



(b)

Figure 20. Specimen preparation: a) Place cotton ball on top of paper; b) Fit cotton into remaining space.

9. Place the plastic lid on top of the cotton ball and ensure that it is securely attached and in the “no vent” position by assuring that the arrows and notches on the cup and cap do not align (Figure 21a).
10. Using the Sharpie, label the sample cup on the top with the sample name or place a circular sticky label with the sample name on the lid. Also write the sample name with a Sharpie on the side of the cup. Finished samples should look like Figure 21b. The foil may be trimmed if desired.
11. Clean the dowel, scoop, and your hands by wiping with a paper towel until no powder is visible. Wipe down the bench area before opening the next sample or use a separate tissue or paper on the bench for each sample. In the case of a sticky or messy sample,

clean dowel, scoop, and hands by washing with water and drying completely before using for the next sample.

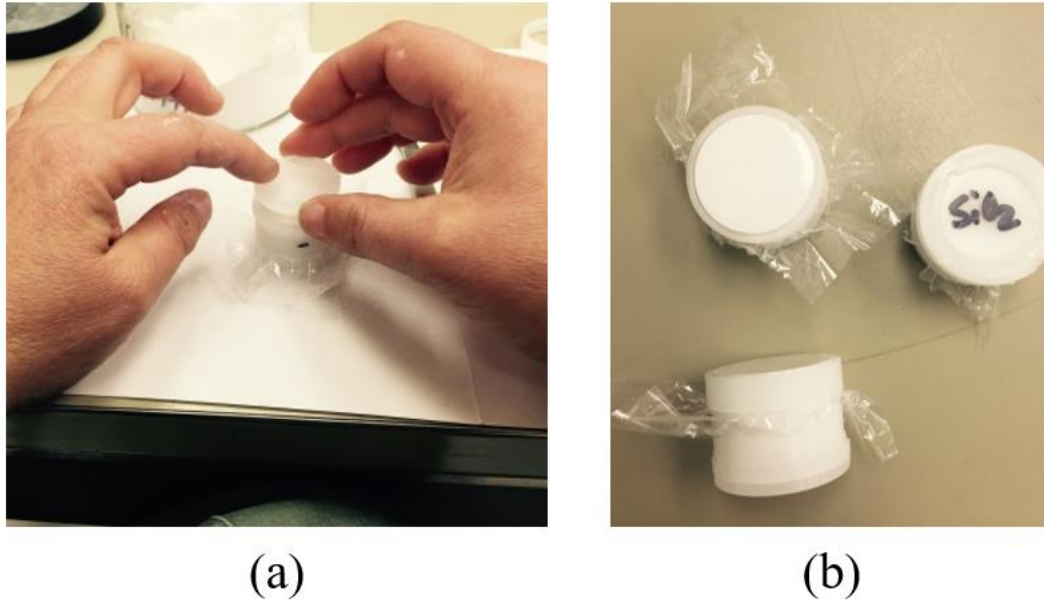


Figure 21. Sample preparation: a) Place lid on top of cotton; b) Finished samples

Once the samples are created, they are ready to test.

Test the untreated and stabilized soil using the GeoMine library with no calibration coefficients. If lime based stabilizers are used, no calibration coefficients are necessary. Portland cement, Cement Kiln Dust, and Fly Ash stabilizers require a coefficient of 1.24 added to the Calcium element. Once the three samples are tested for the calcium content, the stabilizer content can be determined using equation 1. GeoMine reads Calcium content directly. If a comparison is necessary between the PXRF measurement and a fused disc whole rock analysis measurement performed in the lab, then Calcium values must be converted to CaO.

6.2 Proposed Pay Deduction Scale

Pay factors were determined using a performance-based approach, using fixed weighting factors to arrive at a final stabilization pay factor. Popescu and Monismith (2006) have shown that using a relative performance procedure produced similar results as that developed using the more rigorous Monte Carlo approach. The proposed pay deduction factors for stabilization projects are presented in Table 33 and Table 34.

Stabilizer contents (SC) were determined using PXRF testing on specimens prepared according to section 6.1 *Standard Sampling and Testing Procedure and Contractor Specifications*. ΔSC denotes the deviation from the design SC, without regard to sign. Pay adjustments are calculated according to Equation 2:

$$PA = \left(1 - \frac{PF}{100}\right) C_T \quad (2)$$

where

PA is the pay adjustment,

PF is the calculated pay factor,

C_T is the total cost of the stabilization project

Table 33. Proposed pay factors for calcium-based stabilization projects: CKD, FA, PC acceptance schedule

PXRF ΔSC^a	Stabilization Pay Factor
0.0 – 1.9	100
2.0 – 3.9	51 + 12 x ΔSC
4.0 – 5.9	12.5 x ΔSC
> 6.0	Unacceptable ^b

^a ΔSC is the deviation between design and measured stabilizer content

^b Samples tested in this range are unacceptable and shall be removed and replaced at no additional cost to the agency

Table 34. Proposed pay factors for calcium-based stabilization projects: Lime acceptance schedule

PXRF ΔSC^a	Stabilization Pay Factor
0.0 – 0.6	100
0.6 – 1.4	57 + 30 x ΔSC
1.4 – 2.0	25 + 25 x ΔSC
> 2.0	Unacceptable ^b

^a ΔSC is the deviation between design and measured stabilizer content

^b Samples tested in this range are unacceptable and shall be removed and replaced at no additional cost to the agency

Chapter 7: Investigation of Various PXRF Libraries in Detecting Sulfate Content

To test the viability of XRF technology for detecting sulfates in soil, laboratory samples of sulfur-bearing soils were manufactured by mixing a kaolinite soil (Old Hickory Clay, *OHC*) with varying percentages (0 to 100,000 ppm) of laboratory-grade gypsum. Since whole rock analysis reads CaO and SO₃ directly, those values were converted into CaSO₄ using the calculations according to Table 35:

Table 35. Conversions from CaO to Ca and SO₃ to SO₄ to determine sulfate (CaSO₄) content of soils.

Conversion	Formula
CaO to Ca	CaO * 0.7147 = Ca
SO ₃ to SO ₄	SO ₃ * 1.1993 = SO ₄

Table 36. Soil mix design for reference standards to determine sulfate content using PXRF.

Gypsum (ppm)	Gypsum (%)	Sulfate (ppm) ^a	WRA CaO (%)	WRA SO ₃ (%)	WRA CaSO ₄ (%)
100	0.01	56	0.15	0.01	0.12
500	0.05	279	0.16	0.02	0.14
1000	0.10	558	0.17	0.05	0.18
2000	0.20	1116	0.2	0.05	0.20
3000	0.30	1674	0.24	0.12	0.32
4000	0.40	2232	0.28	0.17	0.40
5000	0.50	2790	0.31	0.20	0.46
8000	0.80	4464	0.42	0.29	0.65
10000	1.00	5579	0.50	0.43	0.87
20000	2.00	11159	0.85	0.88	1.66
30000	3.00	16738	1.26	1.27	2.42
40000	4.00	22318	1.49	1.62	3.01
50000	5.00	27897	1.89	2.10	3.87

Gypsum (ppm)	Gypsum (%)	Sulfate (ppm)^a	WRA CaO (%)	WRA SO₃ (%)	WRA CaSO₄ (%)
60000	6.00	33476	2.31	2.56	4.72
70000	7.00	39056	2.50	2.79	5.13
80000	8.00	44635	2.88	3.30	6.02
90000	9.00	50215	3.12	3.41	6.32
100000	10.00	55794	3.55	3.65	6.91

^appm SO₄ = ppm CaSO₄ · 2H₂O x 96.06 g/mol SO₄/172.16856 g/mol gypsum. Rounded to nearest whole number

Three different calibrations were available with the S1 Titan to detect sulfates: Limestone, GeoExploration, and GeoMine. The Limestone calibration optimized for gypsum reads calcium sulfate, or gypsum (CaSO₄), directly. Both GeoMine and GeoExploration calibrations read calcium and sulfur directly, then readings are converted to gypsum in three steps: (i) adding molecular weight of the four oxygen elements, (ii) converting from elemental weight of sulfur to oxide weight using a conversion factor of 2.9956, and (iii) adding the calcium readings to the sulfate calculation, resulting in gypsum (CaSO₄).

Figure 22 shows the results of PXRF readings performed using the standard libraries available without calibration. Laboratory percentages of sulfate (Mixed CaSO₄) were obtained from Whole Rock Analysis (WXRF), which fuses samples on glass discs to provide the actual sulfate values of the mixed samples. These actual values are compared with the measurements obtained using the PXRF on powder samples, and used to calibrate the PXRF. The slopes obtained from Figure 22 can be added to the instrument calibration for calcium (Ca) and sulfur (S) elements and rerun with field and laboratory samples (Figure 23).

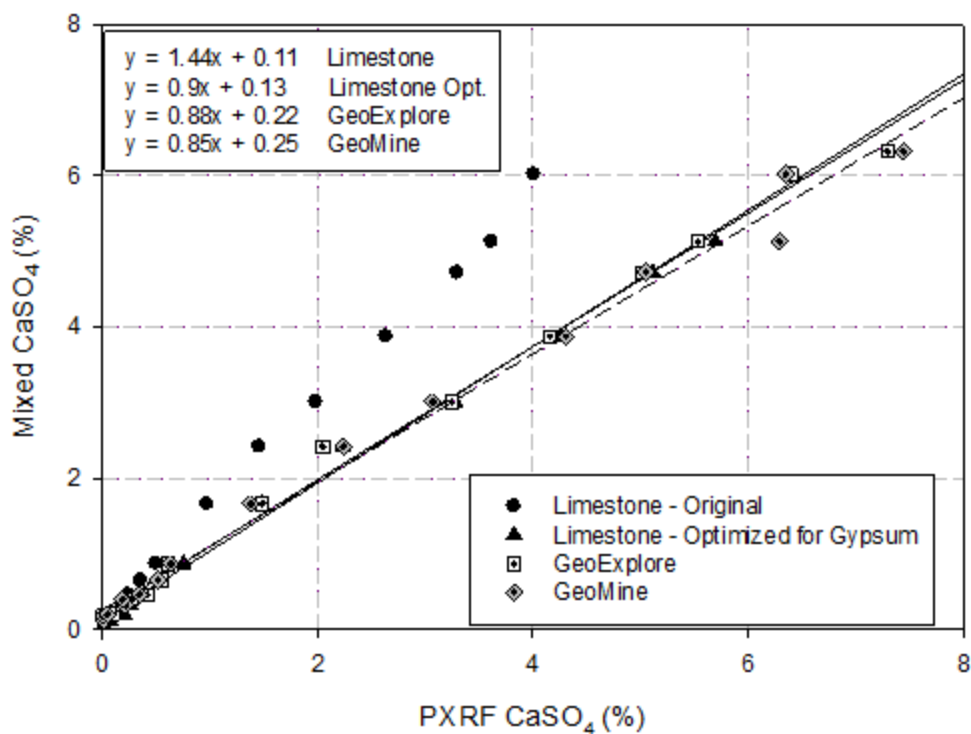


Figure 22. Standard, noncalibrated PXRF Results vs Mixture Percentages

The Limestone calibration, optimized for Gypsum detection (Limestone – Gypsum) standard, even before calibration, accurately determined sulfate content in all reference standards. Additionally, all of the calibrated standards within the PXRF gun (Limestone-Gypsum, GeoExplore and GeoMine) accurately measured the sulfate values from 0 to 8% (Figure 23). Therefore, any of these could be used reliably in the field. With any PXRF protocol, a set of reference standards should be tested first to determine if a calibration factor is needed.

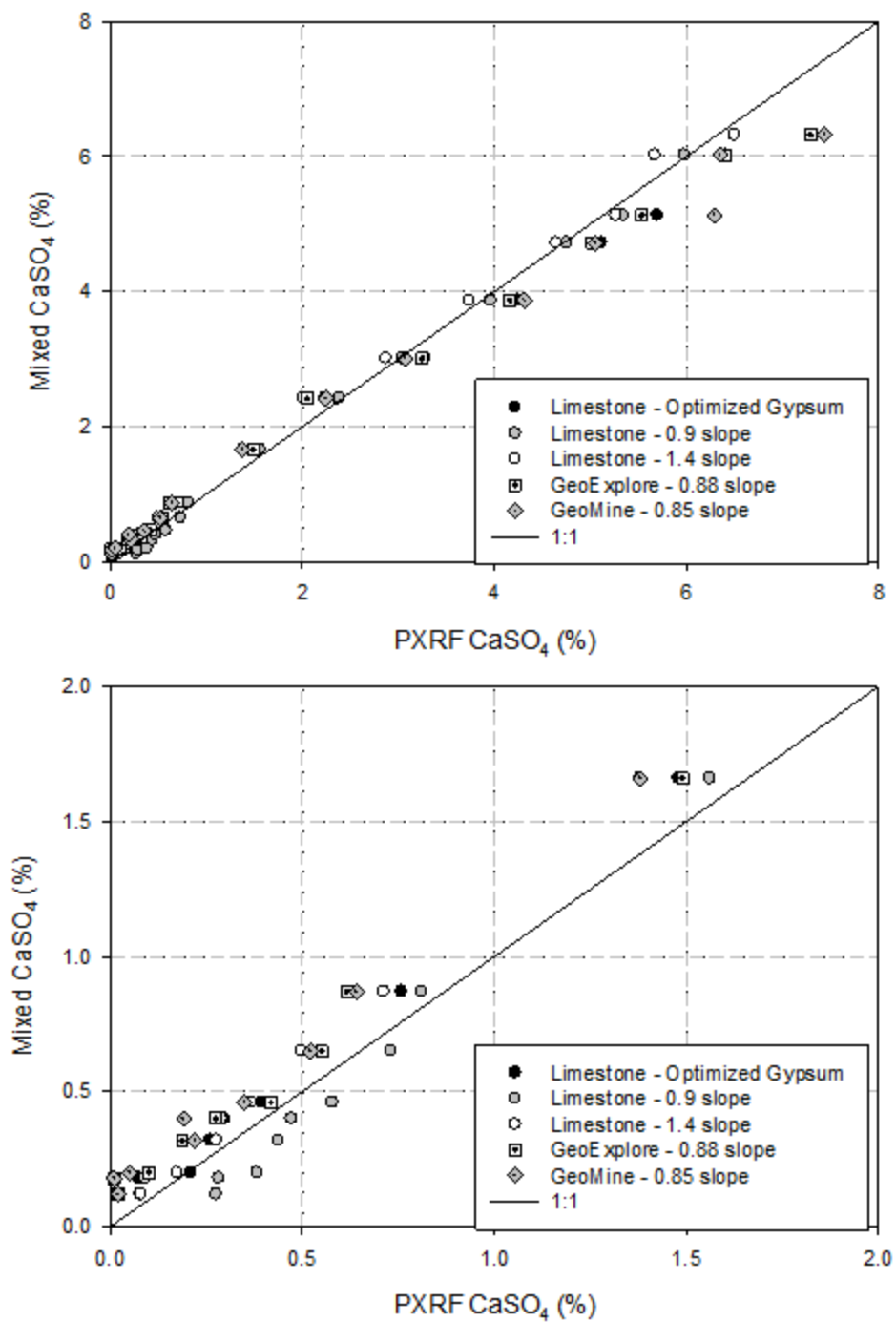


Figure 23. Calibrated Reference Curves using S1 Titan PXRF (top full scale and bottom figure showing only 0-2%).

Chapter 8: Recommendations and Conclusions

8.1 Recommendations

Whole Rock XRF is very advantageous because it melts the sample into a fused disc, removing any particle size effects from the measurements and has been shown to be highly accurate. In addition, commercial labs have a large calibration data set that is refined with additional measurements. This study proved the accuracy of WXRF as a reliable source to evaluate the stabilizer contents in soils mixed with calcium-based stabilizers as well as sulfate contents. However, the drawback of WXRF method is that it is time consuming and can be expensive for a large number of samples.

In this study, the PXRF method was demonstrated to show great promise as a quality control measure for monitoring additive concentration in stabilized soils during construction as well as soil sulfate levels. However, this study also has shown that more refinement of the PXRF method is needed to achieve an acceptable level of accuracy on par with the WXRF method. 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 SCs and sulfates 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.

From this study, the following recommendations are made:

1. When using the PXRF to detect stabilizer content in treated soils, loose powder samples passing the #40 sieve should be scanned for a duration of 60 seconds. Specimens should be prepared according to section 6.1.
2. For detection of calcium-based stabilizers PC, CKD, and FA, the GeoMine library with calibration coefficient 1.24 should be used. For detection of calcium content of lime stabilizers, the GeoMine library with no calibration coefficient should be used.

3. For detection of sulfates in soils, the following reference libraries provide reliable measurements with corresponding calibration coefficients in parentheses: Limestone – Gypsum (no coefficient), Limestone (0.9), Limestone (1.4), GeoExplore (0.88), and GeoMine (0.85)

8.2 Conclusions

The purpose of this research was to evaluate the use of WXRF and PXRF based-methods for determining the additive content in subgrade soils treated with calcium-based chemical stabilizers (lime, fly ash, cement kiln dust and Portland cement), for quality control during construction and for geotechnical forensic investigations. This technology was also used to measure the soil sulfate content. WXRF-based determinations of stabilizer content and gypsum content were made for samples having known additive and sulfate concentrations. The WXRF analysis was performed and used as the basis for the assessment of the PXRF method. Two single-mineral based clays (kaolinite and bentonite) and a silty sand were mixed with four different Calcium-based stabilizers (CaO-based stabilizers) including lime, cement kiln dust, fly ash, and Portland cement at various stabilizer contents (SCs) ranging from 0 to 64%. In addition, the kaolinite was mixed with varying amounts of calcium sulfate ranging from 0 to 10%. The following conclusions were made:

1. The WXRF method was highly accurate and the deviations from the actual stabilizer content (in percent by total weight) were very close to zero. Average magnitude of deviation between actual and WXRF-determined stabilizer content was 0.3% (% by total weight of additive) for a total of 63 samples that were tested.
2. The PXRF method was not as accurate as the WXRF method. Average magnitude of deviation between WXRF-determined and PXRF-determined stabilizer content was 2.1% (% by total weight of additive) for 47 clayey samples. In this comparison, the WXRF values were considered the “true” values of stabilizer content. For a treated sandy soil, the average deviation was 10.6% for 7 samples.
3. Both the WXRF and PXRF methods provided better relative accuracy for higher stabilizer contents.
4. The existing libraries for measuring calcium content (e.g., Limestone-Cement, GeoExplore, GeoMine), measure the lower ranges of Ca in the stabilized soils without

using a slope correction, but do not accurately measure the calcium content of the studied stabilizers (e.g., PC, CKD, FA, and lime) in the higher ranges.

5. Field studies using PXRF show minimal spatial variation in SC applied: both in width and depth.
6. The PXRF, using any available library, was able to accurately detect sulfate in laboratory reference standards for sulfate contents ranging from 0 to 8%. The Limestone-Gypsum (0.9), GeoExplore (0.88), and GeoMine (0.85) libraries showed greater accuracy than Limestone (1.44) for measurement of sulfate contents ranging from 2 to 8%.

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