UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

CALIBRATION OF A HANDHELD X-RAY FLUORESCENCE DEVICE

TO DETECT CHEMICAL STABILIZERS IN SOIL SUBGRADES

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for

the degree of

MASTER OF SCIENCE

CIVIL ENGINEERING

By

THEO VAN HEMELRYCK

Norman, Oklahoma

2018

CALIBRATION OF A HANDHELD X-RAY FLUORESCENCE DEVICE

TO DETECT CHEMICAL STABILIZERS IN SOIL SUBGRADES

A THESIS APPROVED FOR THE

SCHOOL OF CIVIL ENGINEERING AND EVIRONMENTAL SCIENCE

BY

Dr. Gerald Miller, Chair

Dr. Amy Cerato

Dr. Kianoosh Hatami

To friends and family for their supporting love throughout the years and to the many mentors who shared their inestimable knowledge with me,

I dedicate this thesis

ACKNOWLEDGEMENTS

greatly enriched my education and helped me keep my sanity. I would not have completed this

thesis without the help of both. Thank you so much.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMES

CKD: Cement Kiln Dust

CS: Chemical Stabilizer

FA: Fly ash

FPXRF: Field Portable X-Ray Fluorescence

HL: Hydrated Lime

PC: Portland Cement

PHXRF: Portable Handheld X-Ray Fluorescence

OHC: Old Hickory Clay

SC: Stabilizer Concentration

SGB: Super Gel-X Bentonite

SS: Silty Sand

XRF: X-Ray Fluorescence

ABSTRACT

Chemically stabilized subgrades increase the overall quality of pavements compared to non-treated subgrades. Currently, there is no efficient way to detect chemical stabilizers (CS) in pavement subgrades. Generally, only one test indicating the presence of stabilizers is used, however it is rarely mentioned in the design specifications and can only test the presence of stabilizer, not the concentration. Using X-ray fluorescence (XRF) can provide a quantitative measurement of stabilizer content in soils. Previous research at the University of Oklahoma using a Portable Handheld XRF (PHXRF) device showed the need for a unique calibration for chemical stabilizers in soils. Such a calibration can improve measurements of a PHXRF for determining stabilizer content. To create a new calibration, standard samples were made using different soils, chemical stabilizers, and a range of stabilizer content to create a large number of combinations. The method developed with the PHXRF uses the calcium oxide (CaO) concentration measured in raw soil (without CS), CS, and mixed soil (with CS) to determine the amount of CS in the mixed soil. Additionally, an independent laboratory measured the actual CaO content of each sample using the Whole Rock XRF Analysis, which is a validated technique to detect CS in soils. Samples were also subjected to CaO measurement with the PHXRF device for comparison. Through the calibration process, both values, actual (Whole Rock XRF) and experimental (PHXRF), were used to calculate the correction factor to modify the experimental values to best fit the actual ones. This correction factor was used to develop a new calibration. Two validation procedures were performed to determine the accuracy of the new calibration. First, standard samples were subjected to CaO measurement with the PHXRF device using the new calibration to compare to results of the previous values measured during the calibration. Results closer to the

actual values mean that the new calibration improved the device measurement. Other samples not used for the calibration were also prepared and subjected to CaO measurement using the PHXRF device. Two new calibrations were made during this research, one for clay soils and one for sandy soils. The results showed that the PHXRF device provides better CaO content measurements when the coefficients of calibration were applied. The comparison between the new calibrations and the old ones for several samples demonstrated the improvement. The average difference between the SC measurements performed by the device and the actual SC were lower using the new calibrations. However, the new calibration was less accurate than another existing calibration for some high concentration clay samples. Therefore, more studies trying to explain this observation are recommended. Moreover, some additional experiments in the field using the new calibrations are recommended to assess the usability and the accuracy of the new calibrations for quality control purposes. Improving the measurement of SC in soil can significantly improve quality control measures and forensic investigations of pavements leading to increased confidence when stabilizing soils.

Chapter 1

INTRODUCTION

1.1. Overview

1.1.1.   Pavement Subgrades and Chemical Stabilization

The subgrade of a pavement is the in situ soil upon which the pavement structure is placed. That

is, subgrade is the foundation of the pavement; it supports the loads from the pavement and

traffic. The overall pavement performance is significantly related to the subgrade behavior. In the

state of Oklahoma alone, only 64% of major roadways are in decent working condition because

many pavements are built on weak subgrades unable to fulfill their function (Solanki, 2010). One

way to improve the quality of a subgrade is to stabilize it by adding chemicals. Typically, soil

stabilization involves adding a cementitious agent and water to the soil. Many studies show the

efficiency of this technique relative to performance and cost saving (Terrel, Epps and Associates,

1979; Sherwood, 1993; Makusa, 2013). Subgrade stabilization is consequently an important

phase in many pavement construction projects. However, most roadway design specifications

mention no quality control methods other than qualitative methods such as the dye indicator test.

This test only shows the presence of the chemical stabilizer, not its amount (National Lime

Association, 2004). Quantitative tests are rarely mentioned or recommended. In one such test, the

titration test is inconvenient because it requires the user to handle and mix harsh chemicals and is

limited to lime. It also has questionable accuracy due to a large operator bias (Cerato and Miller,

2013). Since correct subgrade stabilization can significantly improve the working condition of

roadways, better quality control measures than those currently used would be an economic

benefit for society as it would save maintenance and repair costs.

1.1.2. Use of X-Ray Fluorescence

An efficient way to detect the concentration of chemical stabilizers in treated soils will have

benefits for the geotechnical profession and the roadway system. Since chemical stabilizers used

for subgrade stabilization are mainly composed of calcium, X-ray fluorescence (XRF) could be a

viable option because it can detect individual elements in materials. By measuring the amount of

calcium in raw soil, raw chemical stabilizer, and treated subgrade soil, XRF can determine the

percentage of calcium coming from the chemical stabilizer in soils (Cerato and Miller, 2013).

Ferraro (2016) used a PHXRF spectrometer to detect chemical stabilizers in different samples.

Despite remarkable linearity of the results, they were too far from the actual values to validate the

method (Ferraro, 2016). One of the reasons is that the calibration library used for the PHXRF

spectrometer in this research was not built specifically for soils and chemical stabilizers.

The research described in this thesis builds upon the work of Ferraro (2016) to improve detection

and quantification of chemical stabilizers in subgrades. This research focuses on creating a new

comprehensive calibration library for a PHXRF device.

1.2. Objectives and Goals

1.2.1. Research Objective

Previous attempts to measure stabilizer content in the field using a PHXRF spectrometer revealed that a new calibration library was needed for the device. In situ testing with the same device compared to a certified method (Whole Rock Analysis) also revealed the need for improved calibration. The main objective of this research is to create a comprehensive library of results for the PHXRF device to create a unique calibration relative to the detection of the stabilizer concentration (SC) in soils. This new calibration module used by the PHXRF spectrometer modifies the device measurement to make results more accurate. Its purpose is to improve the calcium oxide (CaO) measurement accuracy of the PHXRF and consequently improve SC measurement on soils.

1.2.2. Research Goals

The ultimate goals of this research are to benefit the geoengineering profession in two main aspects. Improving the SC measurement could improve quality control during the construction phase of a road project. In fact, using a PHXRF spectrometer is a fast and convenient way to quantify SC in soils. Currently, no such method is used in practice for determining stabilizer contents in treated soils. An efficient way to detect and quantify chemical stabilizers in soil will also benefit forensic investigations. If a pavement structure fails, the PHXRF spectrometer could be a useful tool for quantifying the presence or absence and amount of chemical stabilizer in treated subgrade layers. With such a technique, the liability associated with the amount of chemical stabilizer added to the subgrade during the construction can be addressed. Therefore,

3

investigators would know if the problem is related to chemical stabilizer content or something else.

1.3. Research Tasks

1.3.1. Sample Preparation

Every calibration needs some standards to be used as references. In this research, standard samples are defined as samples with a known concentration of chemical stabilizer. The quality of the calibration significantly depends on the standards used. Therefore, specific attention has been given to the choice of standards and their preparation. The number of standards has to be sufficiently high to have a robust calibration. The concentration of the standard has to be chosen to match realistic conditions. The matrix of standards resulting for this research is presented in Table 6 (Section 3.2.1). Chemical stabilizer concentrations of all samples used for the calibration were determined using the Whole Rock Analysis XRF procedure (Cerato and Miller, 2013) and were conducted by an independent laboratory, ALS Geochemistry, Reno, Nevada. The Whole Rock XRF values are defined as the actual values for the following calibration tasks.

1.3.2. Calibration of X-Ray Device for Chemical Stabilizer

The main task of this research was to create a comprehensive library for the PHXRF spectrometer, in other words, creating a new calibration specific for SC in soils. The calibration procedure is managed by the software Application Wizard provided with the device. Four steps are necessary to complete a new calibration for the PHXRF device.

First, data relative to the materials composing test samples needs to be entered in the software. This means defining the elements the user wants to measure in the samples and eventual compounds linked to these elements. Since chemical stabilizers are mainly composed of calcium, the element desired for the calibration is calcium. Then the standard samples prepared by the user and their respective Ca content are input in the software. For this research standard samples are the ones presented in the testing matrix shown in Table 6 (in Section 3.2.1).

The measurement step is followed by creating a Run Order file which automates the collection of spectra samples. The Run Order will allow the user to collect all the standards measurements of the device in one file. The goal of this step is to collect the measurements from the device so they can be compared to the actual values (standard samples). After the Run Order finishes collecting data, the calibration step calculates a coefficient that will adjust the device's values to align with standard values. The Application Wizard will calculate this coefficient. The next step will be to create a module using this coefficient, which will modify the device's measurement to make it more accurate.

1.3.3. Validation of the Calibration

The efficiency of the new calibration was verified by two different validations. The first validation used the same standards samples used for the calibration. They were again subjected to PHXRF measurement using the new calibration to see if the Ca content values obtained were more accurate than values obtained without the new calibration. The device was also tested using the new calibration on other samples not used for the calibration. Actual calcium concentration was determined for each validation sample by the outside laboratory via Whole Rock XRF.

Measured values were compared with laboratory results to determine if the new calibration gave better results than using the default calibration.

Note that for the calibration phase, Ca content was measured and compared, whereas for the validation phase, CaO content was measured and compared. This difference is because a calibration that can measure CaO content is a dual phase, calibration which is more difficult and time consuming to create and needs more sophisticated software. However, this has no impact on the results because Ca content and CaO content are linearly related by a factor of 1.4 according to Bruker company reference.

Chapter 2

LITERATURE REVIEW

2.1. X-Ray Fluorescence Spectrometry

X-Ray spectrometry principles and applications are discussed in this chapter as well as research already done using PHXRF for treated subgrades. Moreover, methods to calibrate PHXRF devices will be presented.

2.1.1.   Portable X-Ray Fluorescence

History of X-ray fluorescence studies and their applications can be found in Ferraro (2016). These previous studies used laboratory XRF testing to measure the chemical makeup of soils ; however, it is also possible to use XRF analysis in situ. Bernick et al. (1995) first tried to use a field-portable XRF (FPXRF) analysis to measure metal contaminants in soil and sediments. FPXRF analyzers turned out to be a viable, effective approach to meet the on-site metals analysis needs of many hazardous waste site evaluation/removal programs (Bernick et al., 1995). Royon and Taylor (2016) confirmed Bernick et al. (1995) findings that FPXRF is capable of generating reliable, high quality elemental concentration data for metal-contaminated soils. In addition to XRF spectrometry advantages, FPXRF also provides data on-site and hence reduces costs and risks associated with sample transport and storage (Parson et al., 2013). Handheld Portable XRF (PHXRF) is another tool using XRF spectrometry. The FRXRF is a portable bench top device that requires a sample to be prepared whereas the PHXRF can be applied directly to soil in the

field without sampling. An X-ray beam is created by an X-ray tube inside the PHXRF and

emitted from the front end of the device as shown in Figure 1.
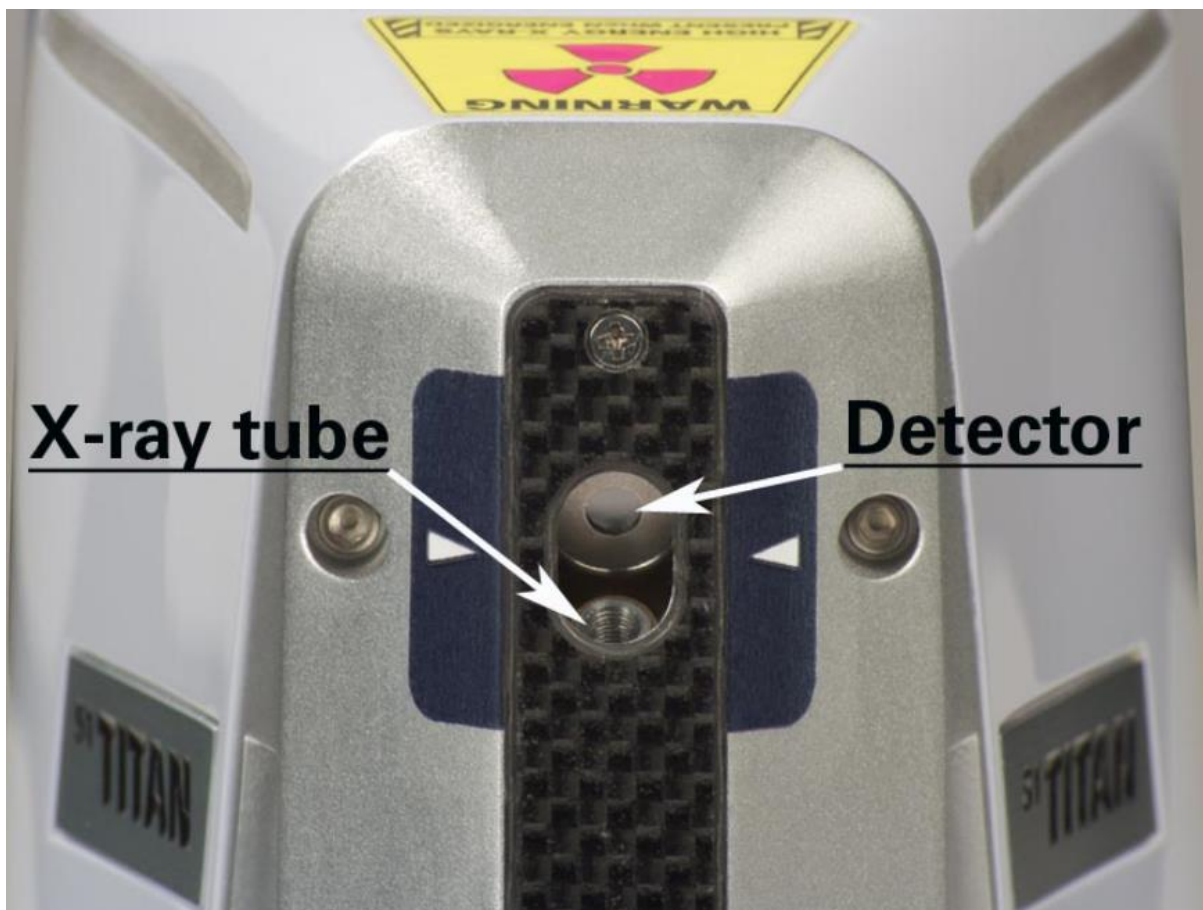
Figure 1: Front end of the TITAN S1 (Bruker 2017)

This X-ray beam interacts with the atoms in the sample area by displacing electrons within the

atoms. Consequently, some electrons will be knocked out of their orbits leaving some "space"

behind them. Then this space will be filled by other electrons from different orbits to balance the

instability. When those replacement electrons move, they will generate a certain amount of

energy and this energy is related to the distance between the orbits, which are unique to each

element. Therefore, the energy lost during the fluorescence can be used to identify elements in the

sample.

Ejected K-shell electron

Incident radiation

M-shell electron
fills vacancy

L-shell electron
fills vacancy

K_β x-ray emitted

K_α x-ray emitted

Shells
(orbits)

K

L

M
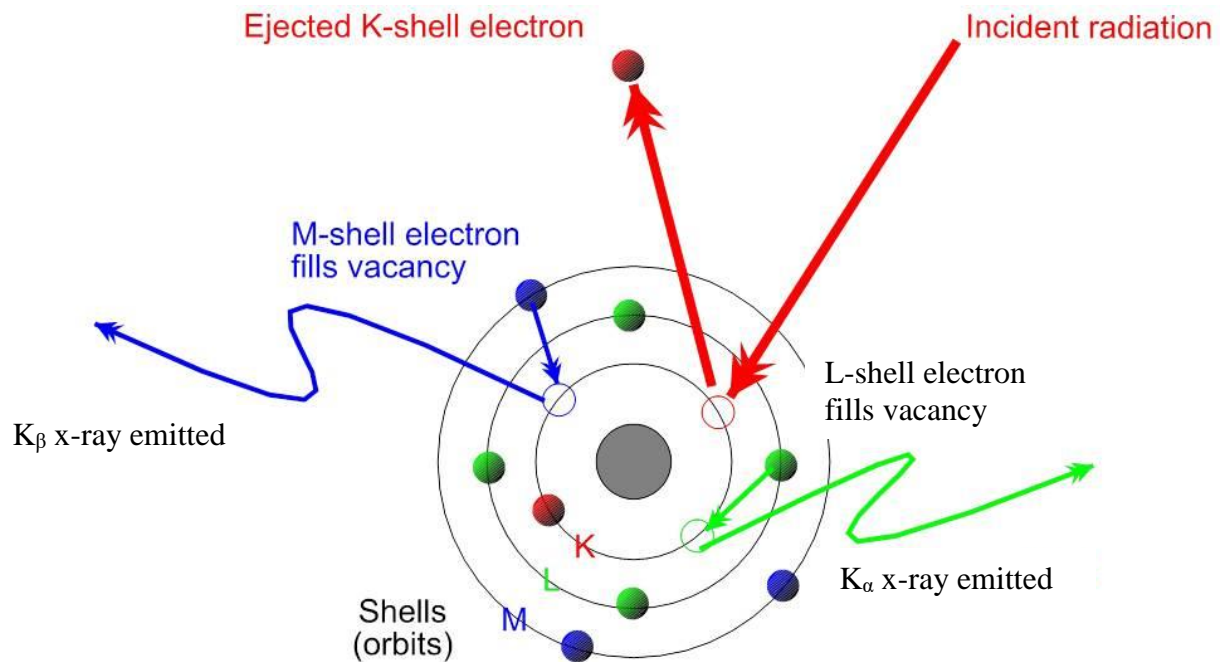
Figure 2: Fluorescence Principle (Bruker 2017)

2.1.2.   Detection of Chemical Stabilizer in Soil

Cerato and Miller (2013) validated a method using Whole Rock XRF to detect the amount of

chemical stabilizer within a stabilized subgrade. They tested several samples from different road

construction sites in order to demonstrate if the XRF technique can accurately measure the

stabilizer content in a soil. Because stabilizers are mainly composed of calcium, they calculated

the stabilizer content by using the calcium oxide content of the stabilized soil, raw soil, and raw

chemical in the following equation:

$$SC = \frac{CaO_f - CaO_0}{CaO_{CA} - CaO_0} \times 100 \qquad (1)$$

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

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

CaO_0 is the amount of CaO measured by XRF in the untreated soil sample (%)

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

However, it is mentioned that the validation of this technique was only accomplished for the "Whole Rock Analysis" performed in a laboratory (Cerato and Miller, 2013). It is also mentioned that a portable field unit using XRF could be a useful tool since it would eliminate the time needed for a laboratory to test the samples.

2.2. PHXRF on Stabilized Subgrades

Ferraro (2016) studied this alternative by testing a handheld portable XRF device (PHXRF) in situ and ex situ. Ferraro (2016) used two different devices, however this study concluded that both devices, Niton XL3t and S1 Titan, may be appropriate for determining SC in stabilized subgrades. The following sections present some results and conclusions obtained by Ferraro (2016).

2.2.1. In Situ Test

In situ testing was defined as measuring the CaO content directly in the soil in the field at several road construction projects. Tests were done directly on the soil surface without any sample preparation. Those tests revealed a poor accuracy of the PHXRF used with no previous sample preparation. This was attributed to the small size of the soil volume involved in the measurement. Therefore, determining SC in subgrade soils by measuring CaO content using the PHXRF without any previous sample preparation is not accurate and consequently not appropriate.

Table 1 shows the randomness of in situ measurements at one of the locations studied by Ferraro (2016). STDEV is the standard deviation between "n" measurements using the device. Coefficient of variation of the standard deviation (COV_{DEV}) assesses the dispersion of the Ca content measurements relative to the mean Ca content. A STDEV and COV_{DEV} close to zero indicates a high precision of the device. The accuracy of the device is indicated by the root-mean-square deviation (RMSD) and the coefficient of variation of the RMSD (COV_{RMSD}). High accuracy is indicated by a RMSD and COV_{RMSD} close to zero.

Table 1: Precision and Accuracy of Niton XL3t In Situ Measurements at Random Grid Locations throughout Site 2 (Ferraro, 2016)

	Location	n	STDEV (%)	COV_{STDEV}	RMSD (%)	COV_{RMSD}
Niton XL3t	4	3	0.534	0.013	19.468	0.953
	16	3	4.139	0.099	20.207	0.925
	27	3	1.857	0.041	32.444	2.435

This low degree of accuracy and precision were confirmed by the linear regression analysis done by Ferraro (2016). As seen in the Figure 3, the large area created between the 95% prediction interval and the 95% confidence interval indicates poor precision of the in situ measurements using PHXRF. The large deviation from the y = x line also proves poor accuracy of those measurements. The low coefficient of determination (R^2) also indicates that the trend line poorly fits the measurements points which means that the data still present large errors even when mathematically corrected.
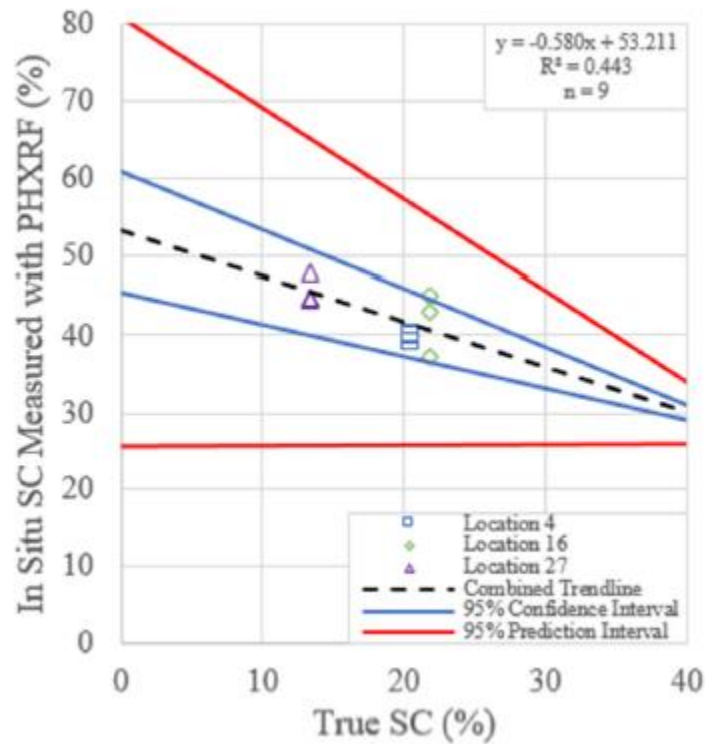
Figure 3: Linear Regression of Site 2 In Situ Measurements with the Niton XL3t PHXRF (Ferraro, 2016)

Note that Table 1 and Figure 3 shows results for the Niton XL3t which a similar device to the S1 Titan. However, Ferraro (2016) mentioned that in situ testing was only performed using Niton

XL3t. Therefore, the accuracy of the S1 Titan for in situ measurements is still unknown but will likely suffer from the same problem of small measurement volume associated with the Niton XL3t device.

2.2.2. Laboratory Testing

For the ex situ testing, Ferraro (2016) made some samples from soils obtained at the same locations used for in situ testing. Several independent variables and their effect on the precision and accuracy of the device were studied. The following sections present some results and conclusion obtained by Ferraro (2016).

Effect of Scan Duration

The scan duration of the measurement using the PHXRF device appeared to have very little effect on the CaO content measurement. Even though some differences in STDEV and RMSD are notable, the lack of variability in COV_{STDEV} and COV_{RMSD} seen in Table 2 for Old Hickory Clay (OHC) Kaolinite indicates these differences were insignificant.

Table 2: Effects of Scan Duration for OHC samples (Ferraro, 2016)

Scan Durations sec (Phase I - Phase II)	n	STDEV %	COV_{STDEV}	RMSD %	COV_{RMSD}
60 (30-30)	270	0.039	0.002	0.850	0.069
60 (15-45)	270	0.027	0.001	0.851	0.069
75 (15-60)	270	0.034	0.001	0.875	0.069
135 (15-120)	270	0.021	0.001	0.876	0.070

Note that similar results were obtained with Super Gel-X Bentonite (SGB) samples (Ferraro, 2016). The linear regression analyses also support the minimal effect of scan duration by showing no difference between the different regression lines as seen in Figure 4.
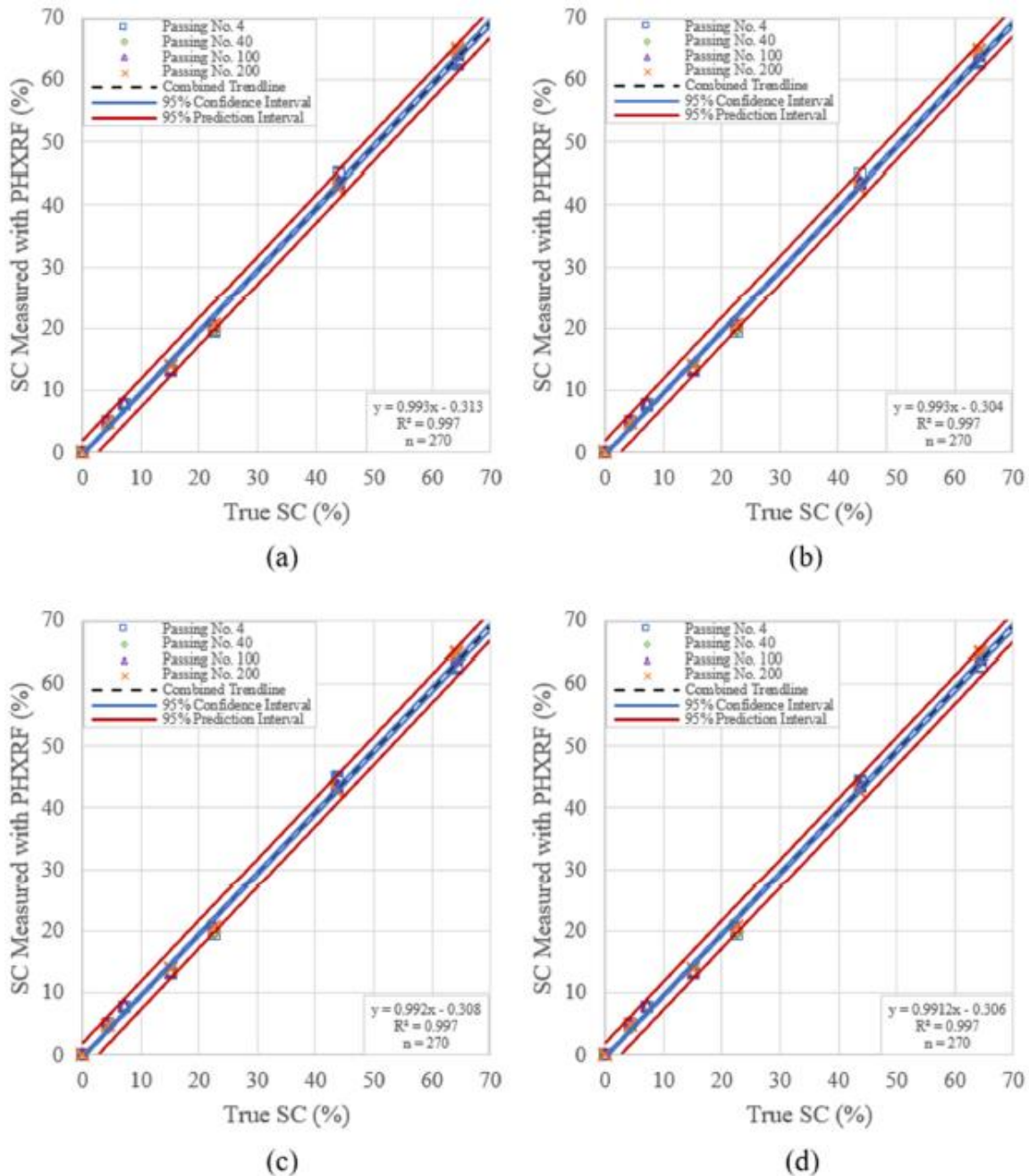
Figure 4: Effects of Different Scan Durations on Precision and Accuracy of PHXRF Device for (a) 60 Second (30-30), (b) 60 Second (15-45), (c) 75 Second (15-60), and (d) 135 Second (15-120) on OHC samples.

Effect of Scan Technique

Scan technique for measurement using the S1 Titan appears to play a role in its precision but a little role regarding its accuracy. Two scan techniques can be used for CaO content measurement using the PHXRF; the standard technique which consists of shooting the sample three times at the same place (usually in the middle) and the quartering technique which consists of shooting every quadrant of the sample three times. The quartering sample technique is shown in Figure 5.
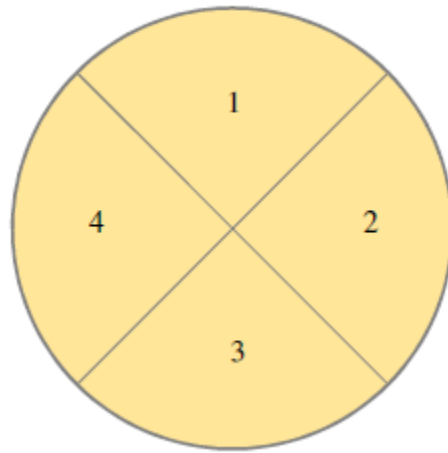
Figure 5: Powder Sample divided in Four Quadrants (Ferraro, 2016)

The standard technique provided more precise results but no significant difference in accuracy was obtained. This improvement of precision is shown in Table 3 by the large difference of STDEV and COV_{STDEV}.

Table 3: Effects of Scan Technique for OHC Samples (Ferraro, 2016)

	Scan Technique	n	STDEV (%)	COV_{STDEV}	RMSD (%)	COV_{RMSD}
S1 Titan	Standard	240	0.029	0.001	2.153	0.133
	Quartering	72	0.254	0.015	2.172	0.140

Particle Size

As shown in Table 4 by the COV_{STDEV}, particle size has no effect on the precision of the CaO content measurement using the PHXRF. However, when the particle size is reduced, the accuracy of the measurements tends to increase as shown by the reduction in COV_{RMSD}.

Table 4: Effects of Size Particle for OHC Samples (Ferraro, 2016)

	Particle Size (Passing)	n	STDEV. (%)	COV_{STDEV}	RMSD (%)	COV_{RMSD}
S1 Titan	No. 4	280	0.035	0.001	1.234	0.082
	No. 40	280	0.025	0.001	0.892	0.062
	No. 100	280	0.024	0.001	0.915	0.077
	No. 200	240	0.036	0.001	0.905	0.056

As seen in Figure 6, benefits to CaO content measurements start to be significant once the sample particle size is reduced passed sieve No. 40. For this reason and to maintain practicality, field samples should be milled to pass sieve No.40.
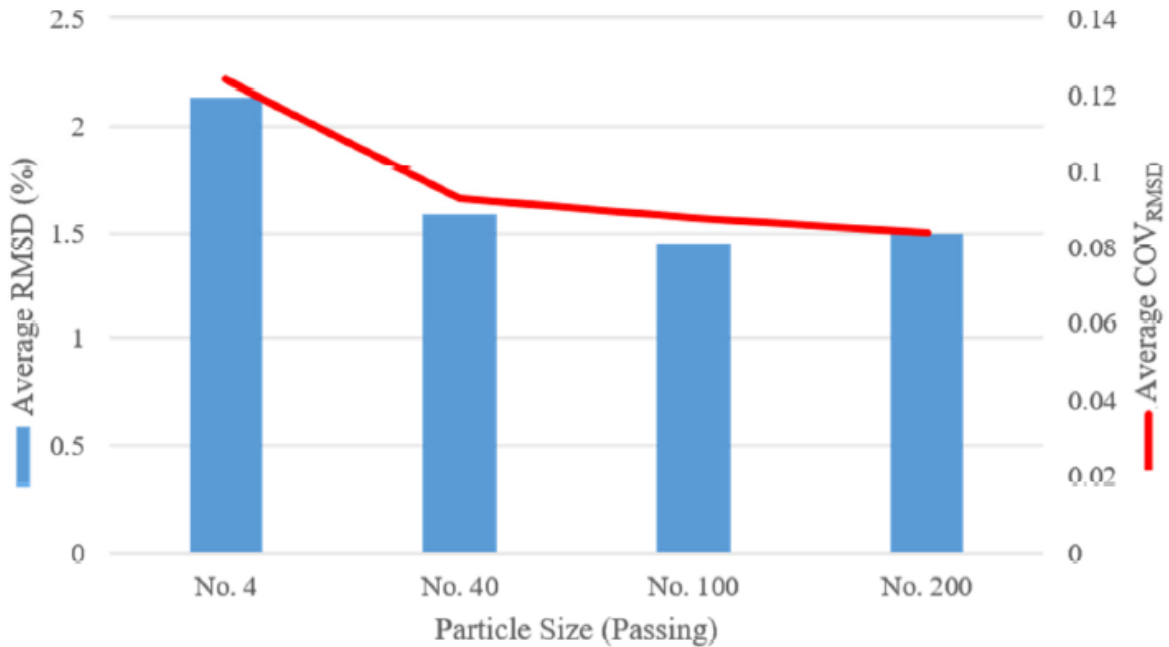
Figure 6: Average RMSD and COV$_{RMSD}$ as a Function of Particle Size (Ferraro, 2016)

Sample Type

Two types of samples were studied; powder and pressed pellet. Ferraro (2016) concluded that the role of sample type on PHXRF accuracy and precision was inconclusive because opposite observations were obtained for OHC samples and SGB samples. The results for OHC samples suggest that pressed pellets produce more accurate measurements whereas results for SGB samples suggest that powder samples produce more accurate measurements. Those opposite results can be seen in Table 5 and Figure 7. Ferraro (2016) indicated that creating a comprehensive reference library relative to chemical stabilizers in soil could improve the application of the PHXRF ex situ measurements. Thus, building on Ferraro's work, this is the purpose of the research described in the remainder of this thesis.

Table 5: Effects of Sample Type for OHC Samples (Top) and SGB Samples (Bottom) (Ferraro, 2016)

	Sample Type	n	STDEV (%)	COV_{STDEV}	RMSD (%)	COV_{RMSD}
S1 Titan	Pellet	240	0.036	**0.001**	**0.905**	**0.056**
	Powder	240	**0.029**	**0.001**	2.153	0.133

	Sample Type	n	STDEV (%)	COV_{STDEV}	RMSD (%)	COV_{RMSD}
S1 Titan	Pellet	280	**0.020**	**0.001**	2.309	0.159
	Powder	280	0.035	0.003	**1.808**	**0.145**
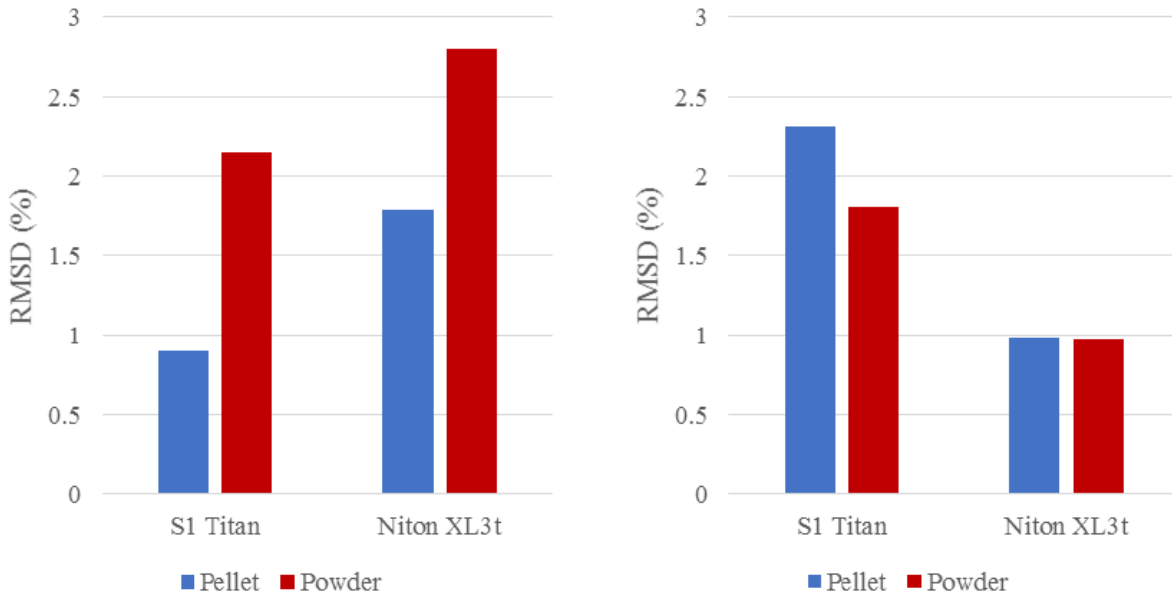
Figure 7: Comparison between Pressed Pellet and Powder Samples for OHC Samples (Left) and SGB Samples (Right) (Ferraro, 2016)

Chapter3

METHODOLOGY

3.1. Materials and Equipment

3.1.1. Soils

This research aimed to create a comprehensive library of stabilized soil results for the PHXRF device. Therefore, samples using different soil types and chemical additives were made. Three soil types, with properties summarized in Table 6, were used for this research:

- *Old Hickory Clay (OHC)* – Kaolinite soil from Hickory, Kentucky,

- *Super Gel-X Bentonite (SGB)* – Absorbent impure bentonite clay from Titan Industries Inc., and

- *Silty Sand (SS)* – Stephenville Sand, Texas.

Table 6: Test Soil Properties

Soil	Passing #10	Passing #40	Passing #200	LL	PI
OHC	100%	100%	98.5%	70	32
SGB	100%	100%	70%	283	39
SS	100%	99.1%	27.7%	N/A	N/A

3.1.2. Chemical Stabilizers

Four different chemical stabilizers, with properties listed in Table 7, were used for this research:

- *Hydrated Lime* – $Ca(OH)_2$ from the Texas Lime Company in Cleburne, Texas,

- *Cement Kiln Dust (CKD)* – Fine, highly alkaline waste removed from cement kiln exhaust Holcim Cement plant in Ada, Oklahoma,

- *Fly Ash Class C*– Fine residue generated in coal combustion from Silver Star Construction Co., Inc. in Moore, Oklahoma, and

- *Portland Cement* – Dolese Type 1 Portland

Table 7: Test Additives Chemical Make up

COMPONENT/PROPERTY	HL	PC	CKD	FA
Silicon dioxide, SiO_2 (%)	<1	21.8	15.6	36.7
Aluminum oxide, Al_2O_3 (%)	---	3.6	3.8	18.6
Iron oxide, Fe_2O_3 (%)	---	2.9	2.1	7.0
SiO2+Al2O3+Fe2O3 (%)	---	28.4	21.4	62.3
Calcium oxide, CaO (%)	>95	63.6	50.6	25.0
Magnesium oxide, MgO (%)	<1	1.9	1.8	5.5
Sulfur trioxide, SO_3 (%)	---	2.5	5.3	1.5
Sodium oxide, Na_2O (%)	---	0.2	0.2	1.8
Potassium oxide, K_2O (%)	---	0.4	3.0	0.5
Loss on ignition (%)	---	2.5	22.1	0.4

3.1.3. Portable Handheld XRF Device (PHXRF)

The PHXRF device used for this research was the S1 TITAN model 600 provided by the Bruker Company. Bruker provides high-performance scientific instruments for scientific usage and notably for XRF analyses. The S1 TITAN is one of the most optimal handheld XRF analyzers available on the market. Indeed, it is among the lightest tube-based PHXRF devices and provides fast and precise XRF analysis (Bruker, 2017). Bruker also provided training videos and sessions, technical documentation and software to the users of the analyzer to insure safety and optimal performance for this research. The S1 TITAN can be handheld or used in a testing stand and triggered remotely, which reduces operator error for ex situ testing and reduces the amount of radiation that can potentially reach the user. Figure 8 shows the device mounted in the testing stand. The device size is 25 cm x 28 cm x 9 cm (10 in x 11 in x 3.7 in) and weighs 1.5 kg (including battery). The X-rays are emitted through a window with dimensions of 10x5 mm and the depth of penetration is about 20 mm. Therefore, the measurement volume involved during the test is 1000 mm^3. The X-ray tube is powered by 50 kV. This model of S1 TITAN can detect 37 elements including Ca and other metals, as well as light elements Mg, Al, and Si.

Figure 8: S1 TITAN from Bruker mounted in the testing stand

3.1.4. Other Lab Materials and Equipment

Other laboratory equipment and materials used in this research included:

- *Water content tins* – tins used to measure gravimetric water content of soils,

- *Milligrams precise scale* – scale with 0.001g resolution,

- *Oven* – used to dry mixed samples,

- *Mortar and pestle* – used to break down dry soil in powder,

- *Single Open-Ended Cups*– cups used as a backing for standard samples subjected to

  PHXRF measurements, and

- *Spectromembrane©* – thin-film support used to close the backing for standard samples

  used for PHXRF measurements,

3.2. Stabilizer Content Definition and Its Determination with PHXRF Measurements of CaO

The amount of stabilizer in a soil can be defined with respect to mass of dry soil or total sample mass (dry soil + chemical stabilizer), and it is important to be consistent when applying these definitions when determining stabilizer content. In engineering practice, the stabilizer content is typically defined with respect to mass of dry soil and is the ratio of the mass of additive (M_{add}) to the mass of dry soil (M_s), as presented in Equation (2).

$$SCs = \frac{Madd}{Ms} \qquad (2)$$

If the stabilizer content is defined in this way, then in order to determine the stabilizer content via CaO content measured by XRF, the correct equation to use is shown as Equation (3).

$$SCs = \frac{CaOf - CaOo}{CaO_{CA} - CaOf} \times 100 \qquad (3)$$

Please note that the denominator of this equation is different than what was presented in Equation (1), as it includes the quantity CaO_f instead of CaO_o. This is because stabilizer content is defined with respect to dry soil in Equation (3). Equation (1) defines stabilizer content with respect to total sample mass, which contains both the mass of dry soil solids and mass of additives, as presented in Equation (4).

$$SC = \frac{Madd}{Mtot} = \frac{Madd}{Ms + Madd} \qquad (4)$$

Defining the stabilizer content with respect to total mass (Equation 4) will always provide a smaller stabilizer content than that defined by mass of dry soil (Equation 2). If this definition, given by Equation (4), is utilized then the stabilizer content can be calculated using Equation (1). Both of these definitions are technically correct, however it is important to know how the stabilizer content is defined at the beginning of the project so as to be able to apply the correct

equation for the measured values post-construction. Data from this project was used to validate these definitions and can be seen in Table 8. For example, for sample name 6*, the stabilizer content, as defined by total mass was mixed to 7.0%. The equation used to calculate how much stabilizer was in the sample based on XRF measured values of CaO, is 6.82%. On the other hand, if the stabilizer content is defined by dry mass of soil solids, the mixed stabilizer content would be defined as 7.53% and the corresponding equation to calculate stabilizer content by using XRF measured values of CaO would be 7.32%. There will always be experimental error between the mixed value of stabilizer content (actual) and the measured value of stabilizer content through XRF, but as seen in Table 8, the differences between actual and measured are very small except for one sample (26*).

Table 8: Comparison of SC and SCs

Name	Madd (g)	Ms (g)	CaO(f) (%)	CaO(O) (%)	CaO(CA) (%)	SC Madd/Mtot (%)	SC Equation 1 (%)	SCs Madd/Ms (%)	SCs Equation 3 (%)
6*	140.00	1860	5.01	0.12	71.85	7.00	6.82	7.53	7.32
14	6	69	5.12	0.12	63.56	8.00	7.85	8.70	8.56
18	4.5	70.5	2.92	0.12	44.75	6.00	6.23	6.38	6.69
19*	300	1700	6.9	0.12	44.75	15.00	15.15	17.65	17.91
25	11.25	63.8	4.02	0.12	25.81	15.00	15.18	17.65	17.90
26*	880	1120	10.61	0.12	25.81	44.00	40.83	78.57	69.01
41	6	69	6.36	1.94	63.56	8.00	7.17	8.70	7.73
46*	240	1760	7.3	1.94	44.75	12.00	12.52	13.64	14.31
47*	420	1580	10.75	1.94	44.75	21.00	20.58	26.58	25.91
51	7.5	67.5	4.14	1.94	25.81	10.00	9.22	11.11	10.15
52	11.25	63.8	5.41	1.94	25.81	15.00	14.54	17.65	17.01
53*	820	1180	11.7	1.94	25.81	41.00	40.89	69.49	69.17
60	6	69	4.75	0.1	63.56	8.00	7.33	8.70	7.91
65	11.25	63.8	6.8	0.1	44.75	15.00	15.01	17.65	17.65
66	17.25	57.8	10.3	0.1	44.75	23.00	22.84	29.87	29.61
70	7.5	67.5	2.51	0.1	25.81	10.00	9.37	11.11	10.34
71	11.25	63.8	3.7	0.1	25.81	15.00	14.00	17.65	16.28
72	33	42	11.04	0.1	25.81	44.00	42.55	78.57	74.07

3.3. Sample Testing Matrix

Standard samples were an important part of the calibration procedure. For this research, several combinations using different soils, chemical stabilizers and concentrations were used to have a sufficiently comprehensive test matrix. Soils and stabilizers listed in the materials section above were used in this matrix. Stabilizer concentrations have been chosen to cover realistic field situations relative to the OHD L-50, which is the design reference for stabilization of roadways in Oklahoma. Therefore, samples were included where SC matches with the OHD L-50 recommendations, where SC is almost null and where SC is two times, or more, greater than the OHD L-50 recommendations. Intermediate concentrations between those three values were also used to make the matrix complete. Previous samples provided by Ferraro (2016) were also used as part of the current test matrix. The resulting calibration matrix is shown in Table 9.

Table 9: Testing Matrix

Soil	Standard Name	Stabilizer	SC targeted (weight %)
OHC	1*	Raw	0
	2	HL	0.5
	3	HL	1
	4	HL	2
	5*	HL	4
	6*	HL	7
	10	PC	0.5
	11	PC	1
	12	PC	2
	13	PC	4
	14	PC	8
	15	CKD	1
	16	CKD	2
	17	CKD	4
	18	CKD	6
	19*	CKD	15
	20*	CKD	23
	21	Fly ash	1
	22	Fly ash	2
	23	Fly ash	5
	24	Fly ash	10
	25	Fly ash	15
	26*	Fly ash	44
	27*	Fly ash	64
SGB	28*	Raw	0
	29	HL	0.5
	30	HL	1
	31	HL	2
	32*	HL	4
	33*	HL	6
	37	PC	0.5
	38	PC	1
	39	PC	2
	40	PC	4
	41	PC	8

Notes:

« Raw » indicates untreated soil

HL: Hydrated lime

PC: Portland Cement

OHC: Old Hickory Clay

SGB: Super Gel-X Bentonite

CKD: Cement Kiln Dust

*: Ferraro (2016) sample

Soil	Standard Name	Stabilizer	SC targeted (weight %)
SGB	42	CKD	1
	43	CKD	2
	44	CKD	4
	45	CKD	6
	46*	CKD	12
	47*	CKD	21
	48	Fly ash	1
	49	Fly ash	2
	50	Fly ash	5
	51	Fly ash	10
	52	Fly ash	15
	53*	Fly ash	41
	54*	Fly ash	63
SS	55	Raw	0
	56	PC	0.5
	57	PC	1
	58	PC	2
	59	PC	4
	60	PC	8
	61	CKD	1
	62	CKD	2
	63	CKD	4
	64	CKD	6
	65	CKD	15
	66	CKD	23
	67	Fly ash	1
	68	Fly ash	2
	69	Fly ash	5
	70	Fly ash	10
	71	Fly ash	15
	72	Fly ash	44
	73	Fly ash	64

Notes:

« Raw » indicates untreated soil

HL: Hydrated lime

PC: Portland Cement

SS: Silty Sand

SGB: Super Gel-X Bentonite

CKD: Cement Kiln Dust

*: Ferraro (2016) sample

3.3.1. Preparation

Ferraro (2016) concluded that the particle size of the samples is important to have a correct measurement from the device. Samples passing the No. 200 sieve turned out to give more accurate values than the other samples with bigger particles size (Ferraro, 2016). However, the difference of accuracy between samples passing No. 200 sieve and samples passing No.40 sieve was relatively small. Therefore, all samples were prepared to pass the No.40 sieve because this particle size is small enough to have good accuracy and more convenient to create with the available materials. Every sample was prepared following the same procedure as Ferraro (2016) and described in subsequent sections. Samples were prepared and tested in an air-dry state.

Moisture Content

The hygroscopic moisture content of each air-dried test soil was determined prior to sample preparation. It was calculated in accordance with ASTM D2216-10 "Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass" for each soil used in this research. Therefore, four metallic tins were filled with the soil and were oven-dried at 110°C for 24 hours. Using the weight difference of the tins before and after being dried, the average gravimetric water content was calculated for each soil. The hygroscopic moisture content obtained for each soil is presented in Table 10. Following moisture content determination, soils were stored in sealed plastic buckets.

Table 10: Hygroscopic Moisture content of Test soils

Soil	Wc (%)
OHC	0.22
OHC 2	1.60
SGB	3.17
SS	0.68

Two different OHC soils are listed in Table 10 because the quantity left in the lab from the previous study was insufficient. Therefore, another bucket of OHC was generously donated by Old Hickory Clay / Gleason Clay Company.

Mass of Stabilizer

The mass of stabilizer needed to reach the desired SC for the standards samples was calculated using Equation (5).

$$Madd = \frac{SC \times Mtot}{100\%} \qquad (5)$$

Where: Madd = Total mass of chemical stabilizer in the sample (moisture ≈ 0%) (g)

Mtot = Total dry mass of the sample (soil plus stabilizer) (g)

SC = Chemical Stabilizer percentage of Mtot (Equation (1), % by weight)

Mass of Soil

The mass of the air-dried soil needed for the sample was calculated using Equation (6)

$$Mm = \frac{Mtot\ (1-\frac{SC}{100\%})}{(1-\frac{wc}{100\%})} \qquad (6)$$

Where: Mm = Total mass of soil in the sample (including hygroscopic moisture) (g)

w_c = Hygroscopic water content of soil (%)

Mixing and pulverizing

Stabilizer and soil masses calculated for each standard were weighed using a milligrams precise scale to be as accurate as possible. Both masses are dry mixed in a metallic bowl, as seen in Figure 9. Water is added and mixed until the mix is homogeneous. The quantity of water added depends on the soil. For OHC, 112 mL is used, 300 mL for SGB and 30 mL for SS. Then the mix is dried in an oven for two days. The temperature in the oven does not exceed 110°F otherwise the mineral structure of the samples could change.
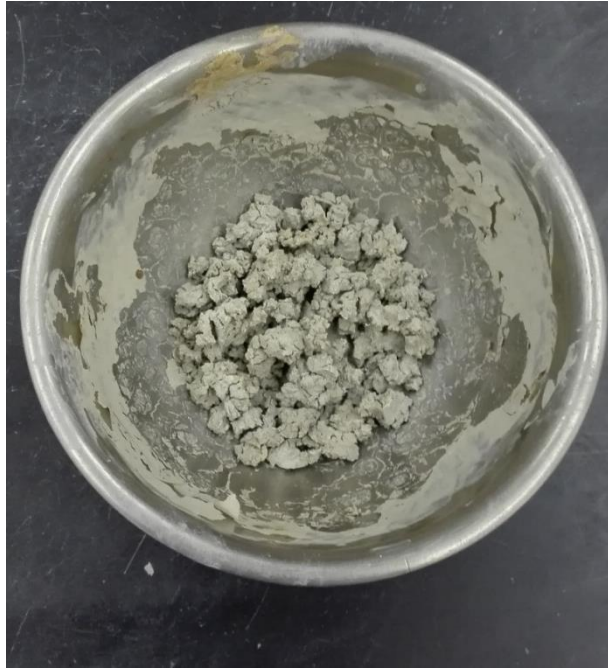
Figure 9: Oven Dried Standard Sample

The dried samples were broken down using a mortar and a pestle until the whole mix passed the

No.40 sieve and placed in a plastic bag as seen in Figure 10.
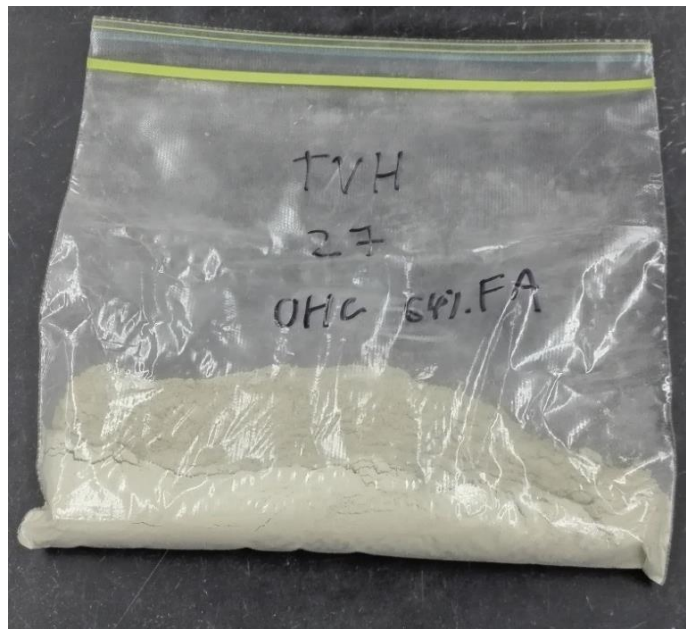
Figure 10: Standard Sample Passing No.40 sieve

Powdered samples

Two type of samples could be used for this research; powdered or pressed pellet samples. Since the type of samples could not be linked to the accuracy of the device (Ferraro, 2016) this current research used powdered samples, which provides a more convenient method with the material available. Plastic films used for sample backing should be thinner than four microns, otherwise the x-rays would not penetrate through it. The thickness of Spectromembrane© used in this study, is two microns which is consistent with this requirement. The backing used for powdered samples needs to be thick enough so that x-rays do not pass through it. That is why no metal of any kind is allowed as the measurement cup material. The measurement cups used for this research are made out of thermoplastic, which is thick enough to not let x-rays penetrate it. The last requirement is that the surface in contact with the gun has to be smooth to have a homogenous dispersion of the x-rays. Single ended cups with collar and rings to tension the Spectromemebrane© were used to satisfy this requirement. Using the material listed before under Lab Materials, the preparation of powdered samples was straightforward. First, 90% of a cup is filled with the sample, a pre-cut Spectromembrane© is placed on the free end of the cup. The user then pushes the first ring down to pre-tension the film and then pushes the second ring fully down to tension the film to have a smooth surface as seen in Figure 11.

Figure 11: Powdered Standard Sample

3.3.2. Standards Samples Matrix

A sample requires 18g to fill a measurement cup, and 24g of sample is needed for ALS to perform whole rock XRF analysis. Therefore, 75g of each sample were made in order to meet that requirement. The mass of additive needed to obtain 75g (dry mass) of mixed sample were calculated using Equation (7). The mass of raw soil (wet mass) needed to obtain 75g (dry mass) of mixed sample was calculated using Equation (8). Each sample was prepared accordingly and sent to ALS Geochemistry after preparation to provide measurements of the actual CaO content in each sample. Calculated additive and wet soil masses needed for each sample, based on water contents in Table 10, are presented in Table 11. Note that every sample with an Asterix on its name is a sample taken from Ferraro (2016) thesis. Ferraro (2016) made 2000g of each sample, therefore Mtot of those samples is not the same than the samples prepared for this research.

Table 11: Standard Samples Matrix

Soil	Standard Name	Stabilizer	SC targeted (weight %)	Wc (%)	Mtot (dry mass in g)	Madd (g)	Mm (wet mass in g)
OHC	1*	Raw	0	0.22	2000	0.00	2004.41
	2	HL	0.5	0.22	75	0.38	74.79
	3	HL	1	0.22	75	0.75	74.41
	4	HL	2	0.22	75	1.50	73.66
	5*	HL	4	1.20	2000	80.00	1943.32
	6*	HL	7	1.20	2000	140.00	1882.59
	10	PC	0.5	1.60	75	0.38	75.84
	11	PC	1	1.60	75	0.75	75.46
	12	PC	2	1.60	75	1.50	74.70
	13	PC	4	1.60	75	3.00	73.17
	14	PC	8	1.60	75	6.00	70.12
	15	CKD	1	1.60	75	0.75	75.46
	16	CKD	2	1.60	75	1.50	74.70
	17	CKD	4	1.60	75	3.00	73.17
	18	CKD	6	1.60	75	4.50	71.65
	19*	CKD	15	1.20	2000	300.00	1720.65
	20*	CKD	23	1.20	2000	460.00	1558.70
	21	Fly ash	1	0.22	75	0.75	74.41
	22	Fly ash	2	0.22	75	1.50	73.66
	23	Fly ash	5	0.22	75	3.75	71.41
	24	Fly ash	10	0.22	75	7.50	67.65
	25	Fly ash	15	0.22	75	11.25	63.89
	26*	Fly ash	44	1.20	2000	880.00	1133.60
	27*	Fly ash	64	1.20	2000	1280.00	728.74
SGB	28*	Raw	0	6.4	2000	0.00	2024.29
	29	HL	0.5	3.17	75	0.38	77.07
	30	HL	1	3.17	75	0.75	76.68
	31	HL	2	3.17	75	1.50	75.91
	32*	HL	4	6.4	2000	80.00	1943.32
	33*	HL	6	6.4	2000	120.00	1902.83
	37	PC	0.5	3.17	75	0.375	77.07
	38	PC	1	3.17	75	0.750	76.68
	39	PC	2	3.17	75	1.500	75.91

Soil	Standard Name	Stabilizer	SC targeted (weight %)	Wc (%)	Mtot (dry mass in g)	Madd (g)	Mm (wet mass in g)
SGB	40	PC	4	3.17	75	3.00	74.36
	41	PC	8	3.17	75	6.00	71.26
	42	CKD	1	3.17	75	0.75	76.68
	43	CKD	2	3.17	75	1.50	75.91
	44	CKD	4	3.17	75	3.00	74.36
	45	CKD	6	3.17	75	4.50	72.81
	46*	CKD	12	6.4	2000	240.00	1781.38
	47*	CKD	21	6.4	2000	420.00	1599.19
	48	Fly ash	1	3.17	75	0.75	76.68
	49	Fly ash	2	3.17	75	1.50	75.91
	50	Fly ash	5	3.17	75	3.75	71.41
	51	Fly ash	10	3.17	75	7.50	67.65
	52	Fly ash	15	3.17	75	11.25	65.84
	53*	Fly ash	41	6.4	2000	820.00	1194.33
	54*	Fly ash	63	6.4	2000	1260.00	748.99
SS	55	Raw	0	0.68	75	0.00	75.51
	56	PC	0.5	0.68	75	0.38	75.14
	57	PC	1	0.68	75	0.75	74.76
	58	PC	2	0.68	75	1.50	74.00
	59	PC	4	0.68	75	3.00	72.49
	60	PC	8	0.68	75	6.00	69.47
	61	CKD	1	0.68	75	0.75	74.76
	62	CKD	2	0.68	75	1.50	74.00
	63	CKD	4	0.68	75	3.00	72.49
	64	CKD	6	0.68	75	4.50	70.98
	65	CKD	15	0.68	75	11.25	64.19
	66	CKD	23	0.68	75	17.25	58.15
	67	Fly ash	1	0.68	75	0.75	74.76
	68	Fly ash	2	0.68	75	1.50	74.00
	69	Fly ash	5	0.68	75	3.75	71.74
	70	Fly ash	10	0.68	75	7.50	67.96
	71	Fly ash	15	0.68	75	11.25	64.19
	72	Fly ash	44	0.68	75	33.00	42.29
	73	Fly ash	64	0.68	75	48.00	27.18

Chapter 4

RESULTS

As discussed previously, calibration of the PHXRF device for stabilized soils involved

determining Ca content of the standard calibration samples using the internal PHXRF calibration

provided with the device. Then, a correction to the internal calibration was developed that is

supposed to make the PHXRF measurements of Ca content closer to the actual values of the

standard samples as determined by Whole Rock XRF. As discussed, the device has internal

software to facilitate the calibration. The evaluation of improvement provided by calibrations

made for determining SC using the S1 TITAN is presented in this section. The improvement

provided by a calibration made during this research was evaluated by calculating the gain of

accuracy provided by the coefficient of calibration applied to the measurements. In addition, the

quality of the standard calibration samples is discussed by comparing the SC targeted during

sample preparation to their actual SC calculated using CaO content measurements from Whole

Rock XRF performed by ALS Geochemistry. The repeatability of the PHXRF is also discussed in

the following sections.

4.1. Standards Quality

In this research, standards quality refers to the difference between the targeted SC during sample preparation and the actual SC obtained using Equation (1) and CaO content measurements from Whole Rock XRF performed by ALS Geochemistry. A difference close to zero suggests a standard sample of high quality. Comparison of targeted SC and actual SC suggest the standard samples are of high quality. The average difference is 0.3% with a maximum difference (delta) of 1.45% and a standard deviation of 0.5%. Note that the highest differences were obtained for samples where the targeted SC was high (from 40% to 60%) and that for samples where targeted SC was low (from 0.5% to 2%), differences were close to zero. Table 12 shows the comparison between targeted SC and actual SC for every standard sample.

Table 12: SC Targeted Compared to Actual SC

Soil	Name	Stabilizer	SC targeted (weight %)	Actual CaO content (%)	Actual SC (%)	Delta (%)
OHC	1*	Raw	0.00	0.12	0	0.00
	2	HL	0.50	0.48	0.50	0.00
	3	HL	1.00	0.82	0.98	0.02
	4	HL	2.00	1.55	1.99	0.01
	5*	HL	4.00	3.04	4.21	0.21
	6*	HL	7.00	5.01	7.05	0.05
	10	PC	0.50	0.45	0.49	0.01
	11	PC	1.00	0.78	1.01	0.01
	12	PC	2.00	1.37	1.94	0.06
	13	PC	4.00	2.62	3.91	0.09
	14	PC	8.00	5.12	7.85	0.15
	15	CKD	1.00	0.64	1.12	0.12
	16	CKD	2.00	1.04	2.02	0.02
	17	CKD	4.00	1.95	4.06	0.06
	18	CKD	6.00	2.92	6.23	0.23
	19*	CKD	15.00	6.9	15.15	0.15
	20*	CKD	23.00	10.3	22.78	0.22
	21	Fly ash	1.00	0.36	0.93	0.07
	22	Fly ash	2.00	0.62	1.95	0.05

Table 12: SC Targeted Compared to Actual SC (Continued)

Soil	Name	Stabilizer	SC targeted (weight %)	Actual CaO content (%)	Actual SC (%)	Delta (%)
	23	Fly ash	5.00	1.39	4.94	0.06
	24	Fly ash	10.00	2.68	9.96	0.04
	25	Fly ash	15.00	4.02	15.18	0.18
	26*	Fly ash	44.00	10.61	40.83	3.17
	27*	Fly ash	64.00	16.4	63.37	0.63
SGB	28*	Raw	0.00	1.94	0	0.00
	29	HL	0.50	2.25	0.44	0.06
	30	HL	1.00	2.58	0.92	0.08
	31	HL	2.00	3.38	2.06	0.06
	32*	HL	4.00	4.45	3.70	0.30
	33*	HL	6.00	6.18	6.30	0.30
	37	PC	0.50	2.13	0.31	0.19
	38	PC	1.00	2.38	0.71	0.29
	39	PC	2.00	2.95		2.00
	40	PC	4.00	4.07	3.46	0.54
	41	PC	8.00	6.36	7.17	0.83
	42	CKD	1.00	2.37	1.00	0.00
	43	CKD	2.00	2.72	1.82	0.18
	44	CKD	4.00	3.55	3.76	0.24
	45	CKD	6.00	4.45	5.86	0.14
	46*	CKD	12.00	7.3	12.52	0.52
	47*	CKD	21.00	10.75	20.58	0.42
	48	Fly ash	1.00	2.26	1.34	0.34
	49	Fly ash	2.00	2.4	1.93	0.07
	50	Fly ash	5.00	3.07	4.73	0.27
	51	Fly ash	10.00	4.14	9.22	0.78
	52	Fly ash	15.00	5.41	14.54	0.46
	53*	Fly ash	41.00	11.7	40.89	0.11
	54*	Fly ash	63.00	17	63.09	0.09
SS	55	Raw	0.00	0.1	0	0.00
	56	PC	0.50	0.41	0.49	0.01
	57	PC	1.00	0.69	0.93	0.07
	58	PC	2.00	1.3	1.89	0.11
	59	PC	4.00	2.48	3.75	0.25
	60	PC	8.00	4.75	7.33	0.67
	61	CKD	1.00	0.54	0.99	0.01

Table 12: SC Targeted Compared to Actual SC (Continued)

Soil	Name	Stabilizer	SC targeted (weight %)	Actual CaO content (%)	Actual SC (%)	Delta (%)
SS	62	CKD	2.00	0.98	1.97	0.03
	63	CKD	4.00	1.83	3.87	0.13
	64	CKD	6.00	2.77	5.98	0.02
	65	CKD	15.00	6.8	15.01	0.01
	66	CKD	23.00	10.3	22.84	0.16
	67	Fly ash	1.00	0.34	0.93	0.07
	68	Fly ash	2.00	0.58	1.87	0.13
	69	Fly ash	5.00	1.3	4.67	0.33
	70	Fly ash	10.00	2.51	9.37	0.63
	71	Fly ash	15.00	3.7	14.00	1.00
	72	Fly ash	44.00	11.04	42.55	1.45
	73	Fly ash	64.00	16.34	63.17	0.83

Actual and targeted SC content are plotted against each other in Figure 12. Linear regression applied to the data in Figure 12 reveals that targeted SC is very close to actual SC. Indeed, the equation of that trend line is y= 0.9949x – 0.0942 with a coefficient of determination (R^2) of 0.9996 which is close to a x=y line.
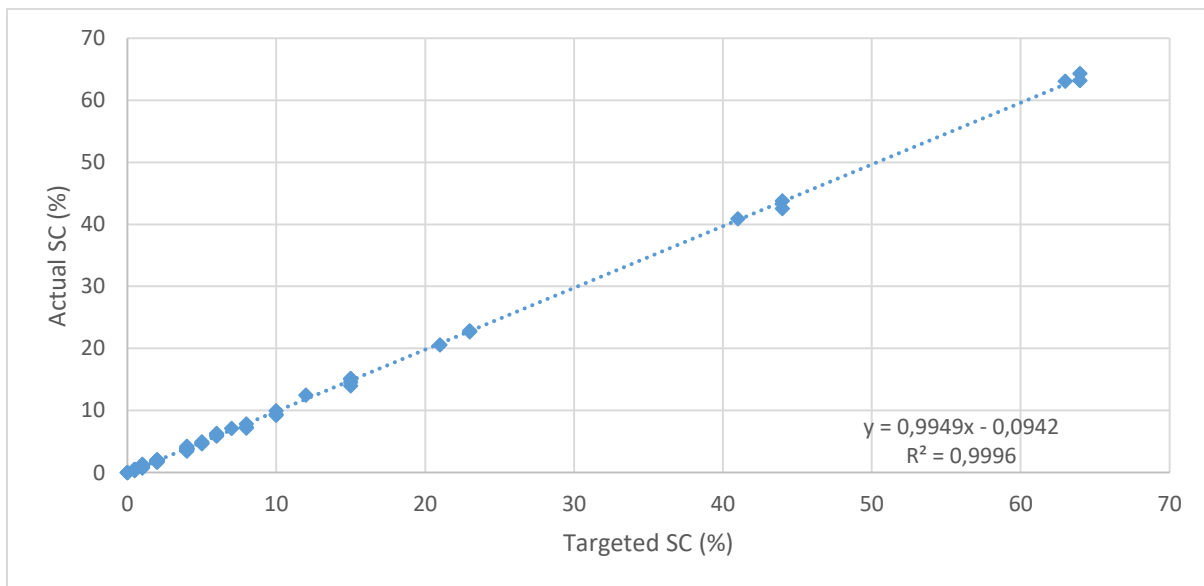
Figure 12: Targeted SC compared to Actual SC for Standard Samples

4.2. PHXRF Repeatability

The repeatability of the PHXRF refers to the difference of measurements from the S1 TITAN using three different sets of calibration measurements and the same standard samples. Note that the calibration measurements are used to determine a correction factor that adjusts the internal calibration provided with the device. A difference between sets of calibration measurements on the same sample that is close to zero suggests good repeatability of the PHXRF device. Repeatability is important for this research to assess the uniformity of the calibration measurements. If repeatability of the device is not good the calibration would not be accurate. Repeatability is a way to assess the precision of the measurements provided by the PHXRF device. The calibration process uses measurements of Ca contents from the PHXRF to create a coefficient of correction to best fit the actual Ca values obtained from ALS laboratories. The Ca content measurements obtained for each of the three calibrations were compared to assess the repeatability of the device. Table 13 shows three repeated sets of calibration measurements (Ca Content 1, 2, and 3) with an average difference between different Ca content measurements of 0.15%, and a standard deviation of 0.37%. Delta 1/2 refers to the difference between the Ca content measured during the first and the second set of calibration measurements. Delta 1/3 refers to the difference between the Ca content measured during the first and the third set of calibration measurements. Delta 2/3 refers to the difference between the Ca content measured during the second and the third set of calibration measurements.

Table 13: Comparison of Repeated Ca Content Measurements using the S1 TITAN

Standard Name	Actual Ca content (%)	Ca Content 1 (%)	Ca Content 2 (%)	Ca Content 3 (%)	Delta 1/2 (%)	Delta 1/3 (%)	Delta 2/3 (%)
2	0.48	0.66	0.68	0.67	0.02	0.01	0.01
3	0.82	1.00	1.02	1.008	0.02	0.01	0.01
4	1.55	1.81	1.85	1.847	0.04	0.04	0.00
5	3.04	3.24	3.25	3.288	0.01	0.05	0.04
6	5.04	5.17	5.17	5.236	0.00	0.07	0.07
10	0.45	0.57	0.59	0.599	0.01	0.03	0.01
11	0.78	0.91	0.92	0.929	0.01	0.02	0.01
12	1.37	1.45	1.45	1.482	0.00	0.03	0.03
13	2.62	2.65	2.64	2.68	0.01	0.03	0.04
14	5.12	4.92	4.96	4.98	0.04	0.06	0.02
15	0.64	0.71	0.71	0.696	0.00	0.01	0.02
16	1.04	1.11	1.09	1.1	0.02	0.01	0.01
17	1.95	1.78	1.80	1.956	0.02	0.18	0.16
18	2.92	2.62	2.54	2.593	0.08	0.03	0.05
21	0.36	0.48	0.46	0.468	0.02	0.01	0.01
22	0.62	0.73	0.69	0.695	0.04	0.03	0.00
23	1.39	1.45	1.42	1.476	0.03	0.03	0.05
24	2.68	2.70	2.67	2.645	0.03	0.06	0.02
25	4.02	3.91	3.90	3.923	0.01	0.02	0.02
29	2.25	2.63	2.54	2.636	0.09	0.01	0.10
30	2.58	3.02	3.05	3.099	0.03	0.08	0.05
31	3.38	3.62	3.61	3.724	0.02	0.10	0.12
37	2.13	2.31	2.28	2.299	0.02	0.01	0.02
38	2.38	2.57	2.52	2.492	0.04	0.07	0.03
39	2.95	3.48	3.46	3.514	0.02	0.04	0.06
40	4.07	4.60	4.52	4.457	0.09	0.14	0.06
41	6.36	7.36	7.59	7.778	0.23	0.42	0.19
42	2.37	2.56	2.43	2.536	0.13	0.02	0.10
43	2.72	3.41	3.25	3.272	0.16	0.13	0.02
44	3.55	4.73	4.73	4.641	0.01	0.08	0.09
45	4.45	4.71	4.71	4.725	0.00	0.01	0.01
48	2.26	2.54	2.47	2.513	0.06	0.02	0.04
49	2.4	2.88	2.82	2.916	0.06	0.03	0.09
50	3.07	3.18	3.31	3.295	0.13	0.12	0.01
51	4.14	4.68	4.78	4.816	0.09	0.13	0.04
52	5.41	5.64	5.72	5.726	0.08	0.09	0.01

Table 13: Comparison of Ca Content Measurements using the S1 TITAN (Continued)

Standard Name	Actual Ca content (%)	Ca Content 1 (%)	Ca Content 2 (%)	Ca Content 3 (%)	Delta 1/2 (%)	Delta 1/3 (%)	Delta 2/3 (%)
55	0.1	0.30	0.29	0.274	0.01	0.03	0.02
56	0.41	1.32	1.09	1.08	0.23	0.24	0.01
57	0.69	1.78	1.81	1.65	0.04	0.13	0.16
58	1.3	3.09	3.37	3.321	0.28	0.23	0.05
59	2.48	5.26	5.83	5.712	0.57	0.45	0.12
60	4.75	9.38	9.59	10.35	0.21	0.97	0.76
61	0.54	1.09	1.04	1.1	0.06	0.01	0.07
62	0.98	2.08	2.12	2.109	0.04	0.03	0.01
63	1.83	3.39	3.55	3.523	0.16	0.14	0.02
64	2.77	4.31	4.25	4.272	0.05	0.03	0.02
65	6.8	10.82	11.36	11.395	0.53	0.57	0.04
66	10.3	13.88	14.96	11.336	1.08	2.55	3.63
67	0.34	0.84	0.77	0.864	0.08	0.02	0.10
68	0.58	1.46	1.36	1.466	0.10	0.01	0.11
69	1.3	2.79	2.59	2.638	0.20	0.15	0.05
70	2.51	4.93	4.89	5.037	0.04	0.11	0.15
71	3.7	7.15	7.89	7.041	0.74	0.11	0.85
72	11.04	16.72	15.63	16.228	1.10	0.49	0.60
73	16.34	19.89	19.65	19.813	0.24	0.07	0.17
				Average	0.13	0.16	0.16

A comparison of actual Ca content and Ca content determined with each of the three calibration data sets is represented in Figure 13. The linear regression also demonstrates the repeatability of the device. Only small differences are visible between the three trend lines of each calibration using the same set of samples. The equations of those trend lines are similar, and the difference is insignificant. Note that Figure 13 reveals the difference between the actual Ca content and the Ca content using the internal calibration provided with the device. The repeatability with the internal calibration is good, as discussed; however, the difference between the trend lines and the 1:1 line

indicates an adjustment to the internal calibration is needed to improve the accuracy of the

measurements. This is discussed in the following sections.
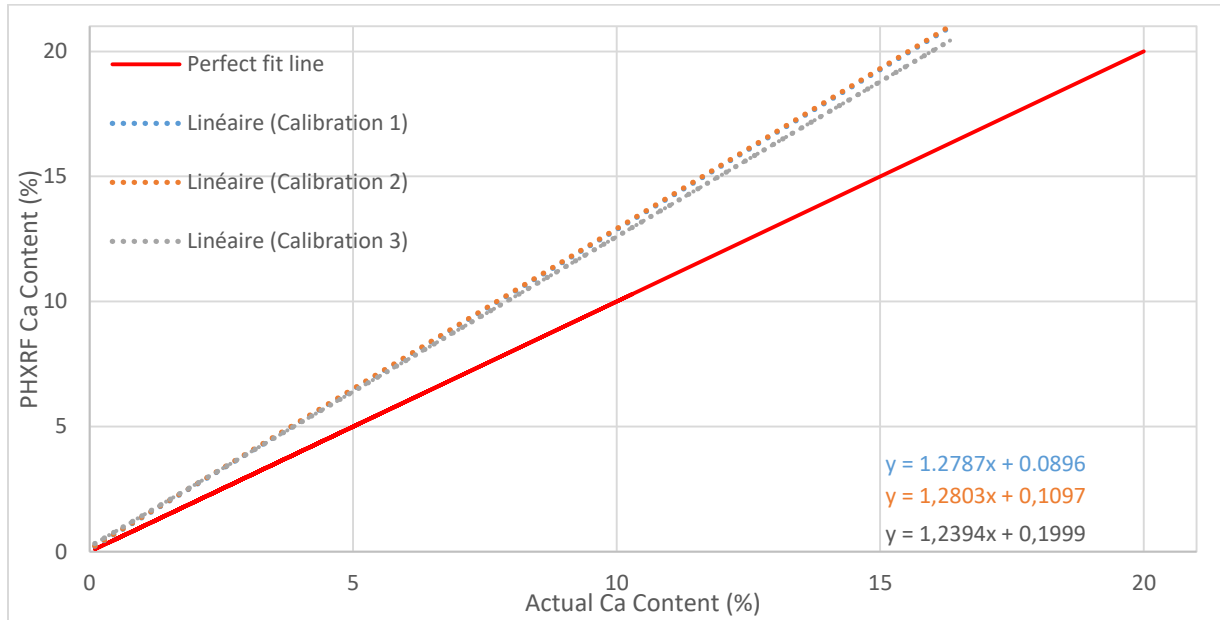
Figure 13: Comparison of Three Different Sets of Ca content Measurements for Calibration using S1 TITAN on the same Set of Standard Samples

4.3. Global Calibration

Global calibration refers to the calibration made using all the standard samples. That is, clay

standards (OHC and SGB) and sand standards (SS) prepared previously were used to determine a

single calibration for all the three soil types. This calibration included measurements on 55

samples with three soils and four chemical stabilizers. This was the first calibration made during

this research, its goal was to assess the feasibility of a single calibration containing every soil and

additive type. The following sections present the results of this calibration and the conclusions

deduced.

4.3.1.   Global Calibration Improvement

The improvement of the calibration refers to the difference between the original measurements provided by the PHXRF during the calibration process and the modified values obtained by applying the calibration coefficient. The average deviation with and without the coefficient of calibration applied to the Ca content measurements using the PHXRF are compared. In this research the deviation refers to the difference between the actual Ca content of the samples and the Ca content measurement provided by the S1 TITAN. No improvement to the PHXRF accuracy was observed during the global calibration. Indeed, the coefficient of calibration, calculated by the Application Wizard, applied to the PHXRF measurements increased the average standard deviation, but by an insignificant amount. The average Ca content deviation is 0.86% without the coefficient applied against 0.87% with the coefficient applied. Therefore, the coefficient of calibration does not generally improve the PHXRF measurements. However, the calibration did improve the measurements for some of the samples. As seen in Table 14, OHC measurements were worsened whereas measurements for SS and some SGB samples were improved. In Table 14, the column "Delta" refers to the difference of deviation between original Ca content and modified Ca content. "Original Ca content" and "Modified Ca content" refer respectively to the Ca content measurement using the PHXRF without and with the coefficient of calibration applied. Green highlighted delta indicates an improved accuracy whereas a non-highlighted delta indicates worsened accuracy.

Table 14: Standard Deviation with and without the Coefficient of Calibration Applied, Comparison for Global Calibration

Standard Name	Soil	Actual Ca content (%)	Original Ca content (%)	Deviation (%)	Modified Ca content (%)	Deviation (%)	Delta (%)
1*	OHC	0.09	0.26	0.17	-0.25	0.33	-0.16
2	OHC	0.34	0.473	0.133	-0.127	0.467	-0.334
3	OHC	0.59	0.716	0.126	0.122	0.468	-0.342
4	OHC	1.11	1.293	0.183	0.716	0.394	-0.211
5*	OHC	2.17	2.317	0.147	1.768	0.402	-0.255
6*	OHC	3.58	3.693	0.113	3.183	0.397	-0.284
10	OHC	0.32	0.408	0.088	-0.194	0.514	-0.426
11	OHC	0.56	0.649	0.089	0.053	0.507	-0.418
12	OHC	0.98	1.034	0.054	0.449	0.531	-0.477
13	OHC	1.87	1.892	0.022	1.331	0.539	-0.517
14	OHC	3.66	3.513	0.147	2.998	0.662	-0.515
15	OHC	0.46	0.507	0.047	-0.093	0.553	-0.506
16	OHC	0.74	0.79	0.05	0.199	0.541	-0.491
17	OHC	1.39	1.271	0.119	0.693	0.697	-0.578
18	OHC	2.09	1.875	0.215	1.314	0.776	-0.561
19*	OHC	5.95	4.27	1.69	2.63	3.32	-1.63
20*	OHC	8.87	6.97	1.90	3.91	4.96	-3.06
21	OHC	0.26	0.342	0.082	-0.263	0.523	-0.441
22	OHC	0.44	0.52	0.08	-0.079	0.519	-0.439
23	OHC	0.99	1.035	0.045	0.45	0.54	-0.495
24	OHC	1.92	1.932	0.012	1.372	0.548	-0.536
25	OHC	2.87	2.791	0.079	2.255	0.615	-0.536
26*	OHC	7.58	6.75	0.83	6.65	0.93	-0.10
27*	OHC	11.08	9.77	1.31	5.81	5.27	-3.96
28*	SGB	1.39	1.31	0.08	1.19	0.19	-0.12
29	SGB	1.61	1.877	0.267	1.316	0.294	-0.027
30	SGB	1.84	2.161	0.321	1.607	0.233	0.088
31	SGB	2.42	2.59	0.17	2.048	0.372	-0.202
32*	SGB	3.18	3.56	0.38	3.51	0.33	0.05
33*	SGB	4.41	4.71	0.29	4.69	0.28	0.02
37	SGB	1.52	1.649	0.129	1.081	0.439	-0.31
38	SGB	1.7	1.833	0.133	1.271	0.429	-0.296
39	SGB	2.11	2.485	0.375	1.941	0.169	0.206
40	SGB	2.91	3.289	0.379	2.767	0.143	0.236
41	SGB	4.55	5.259	0.709	4.793	0.243	0.466
42	SGB	1.69	1.829	0.139	1.267	0.423	-0.284

Table 14: Standard Deviation with and without the Coefficient of Calibration Applied,
Comparison for Global Calibration (Continued)

Standard Name	Soil	Actual Ca content (%)	Original Ca content (%)	Deviation (%)	Modified Ca content (%)	Deviation (%)	Delta (%)
43	SGB	1.94	2.434	0.494	1.888	0.052	0.442
44	SGB	2.54	3.377	0.837	2.858	0.318	0.519
45	SGB	3.18	3.366	0.186	2.846	0.334	-0.148
46*	SGB	6.08	6.77	0.70	6.82	0.74	-0.05
47*	SGB	9.12	10.11	0.99	10.25	1.13	-0.14
48	SGB	1.62	1.813	0.193	1.25	0.37	-0.177
49	SGB	1.72	2.06	0.34	1.504	0.216	0.124
50	SGB	2.19	2.272	0.082	1.722	0.468	-0.386
51	SGB	2.96	3.347	0.387	2.827	0.133	0.254
52	SGB	3.87	4.028	0.158	3.527	0.343	-0.185
53*	SGB	7.86	7.52	0.34	7.58	0.28	0.06
54*	SGB	11.36	10.62	0.74	10.78	0.58	0.16
55	SS	0.07	0.217	0.147	-0.39	0.46	-0.313
56	SS	0.29	0.943	0.653	0.355	0.065	0.588
57	SS	0.49	1.269	0.779	0.691	0.201	0.578
58	SS	0.93	2.211	1.281	1.659	0.729	0.552
59	SS	1.77	3.761	1.991	3.253	1.483	0.508
60	SS	3.39	6.702	3.312	6.276	2.886	0.426
61	SS	0.39	0.779	0.389	0.187	0.203	0.186
62	SS	0.7	1.488	0.788	0.916	0.216	0.572
63	SS	1.31	2.421	1.111	1.875	0.565	0.546
64	SS	1.98	3.077	1.097	2.549	0.569	0.528
65	SS	4.86	7.736	2.876	7.339	2.479	0.397
66	SS	7.36	9.922	2.562	9.586	2.226	0.336
67	SS	0.24	0.601	0.361	0.004	0.236	0.125
68	SS	0.41	1.041	0.631	0.457	0.047	0.584
69	SS	0.93	1.995	1.065	1.437	0.507	0.558
70	SS	1.79	3.521	1.731	3.005	1.215	0.516
71	SS	2.64	5.113	2.473	4.642	2.002	0.471
72	SS	7.89	11.951	4.061	11.672	3.782	0.279
73	SS	11.68	14.213	2.533	13.997	2.317	0.216
74	HL	51.35	54.256	2.906	55.163	3.813	-0.907
76	CKD	31.98	28.564	3.416	28.751	3.229	0.187
77	FA	18.45	18.884	0.434	18.799	0.349	0.085
78	PC	45.43	38.064	7.366	38.517	6.913	0.453
79	OHC	0.1	0.344	0.244	-0.26	0.36	-0.116

The linear regression shown in Figure 14 also shows the lack of improvement using the global calibration. The trend line generated by the modified data is further from the y=x line than the trend line generated using the original data. The coefficient of calibration improved the Ca measurements for Ca concentrations greater than 3% and worsened other measurements. Since the majority of the standards have a Ca content lower than 3%, the improvement was not observed for the majority of the measurements. Moreover, the improvement observed is not large enough to be considered significant.
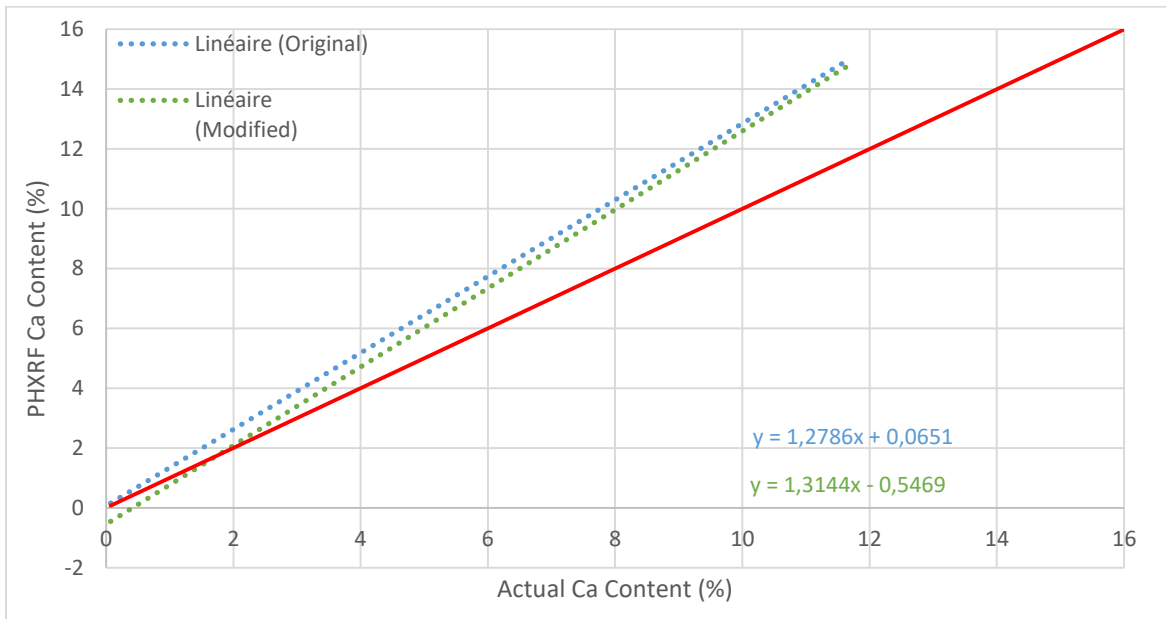
Figure 14: Ca Content Measurements against Actual Ca Content for Global Calibration with and without the Coefficient of Calibration applied.

Global improvement in the measurements was not achieved using all the samples together. However, Table 14 shows that the global calibration tends to improve the measurements performed by the PHXRF for almost every SS sample and half of SGB samples whereas it worsened all measurements for OHC samples. Regrouping the Ca content measurements done by the PHXRF during the global calibration by type of soil revealed a strong relationship between

47

the PHXRF measurement accuracy and the type of soil used in standard samples. Qualitatively speaking, the measurements obtained with the S1 TITAN were quite good for SGB samples, reasonably good for OHC samples, especially for low Ca content, and not as good for the SS samples. Figure 15 presents these observations by showing the data plotted by type of soil. Note that purple data points on Figure 15 identify Ferraro's (2016) samples and the red line on each chart is the x=y line.
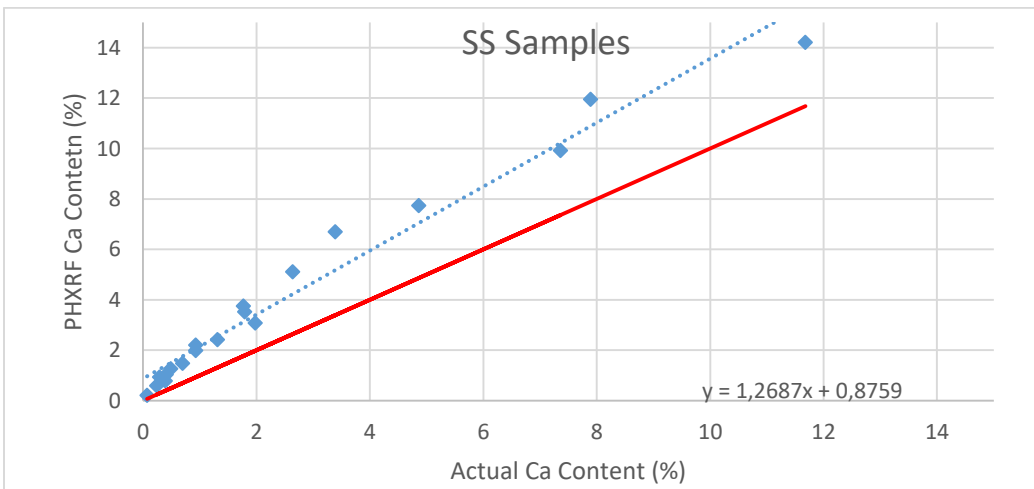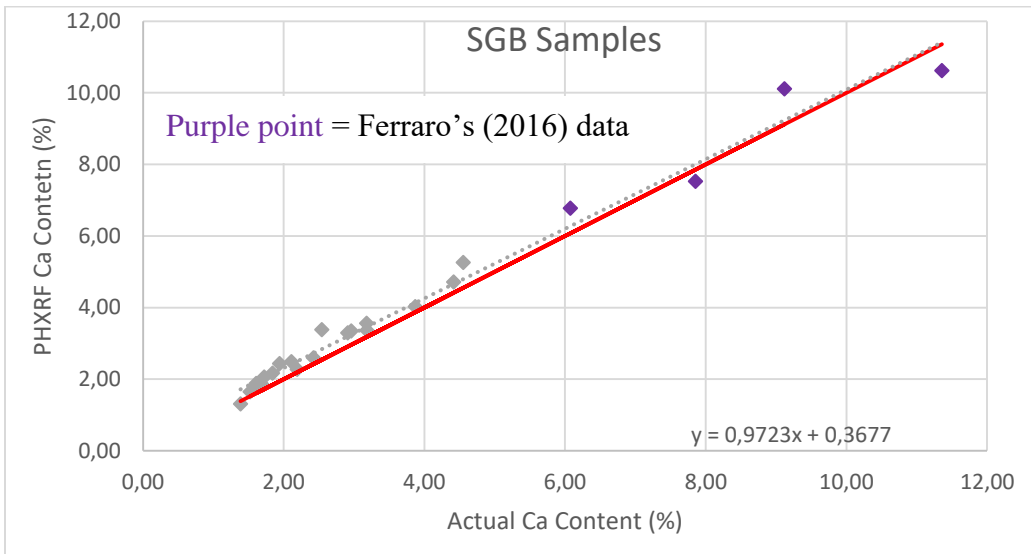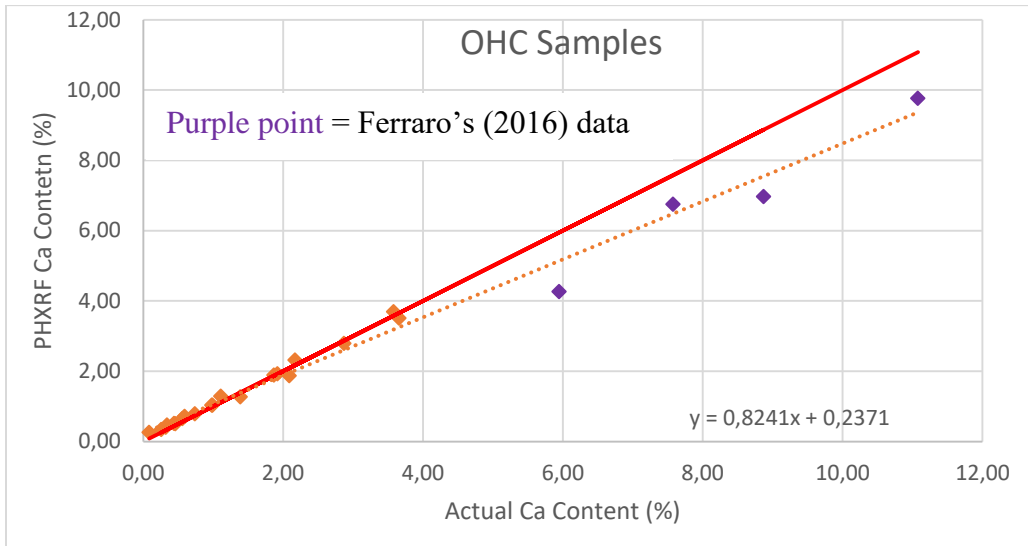
Figure 15: Ca Content Measurements Performed by S1 TITAN during the Global Calibration grouped by Soil Type

49

The results on Figure 15 suggest that the size of the soil particles influences the accuracy of the PHXRF measurements. Indeed, SGB has the finest particles and the most accurate measurements using the internal calibration of the device. Sand samples are the furthest from the actual Ca content and has the largest particles.

4.3.2. Summary of Findings from the Global Calibration Exercise

The global calibration showed that using all the standard samples in a single calibration does not lead to a significant improvement of the Ca content measurement accuracy provided by the PHXRF compared to the initial calibration that comes with the device. However, regrouping the data provided during this global calibration showed that the type of soil significantly influenced the accuracy of measurements from the device. Therefore, different calibrations relative to each type of soils should lead to a better improvement than the one obtained with the global calibration. The conclusion deduced from this first calibration was that other calibrations specific for each type of soil were needed. Even though there was a notable accuracy difference between OHC and SGB samples with high Ca content, both gave reasonably accurate measurements using the internal calibration of the device, particularly at Ca contents less than 6%. Therefore, a single calibration using the samples made with those two types of soil was performed. Another calibration using only SS sand samples was also performed to compare the results with the global calibration.

4.4. Clay Calibration

Clay calibration refers to the calibration done with OHC samples and SGB samples only.
Therefore, 48 samples were used for this calibration. The improvement provided by this
calibration is discussed in the following sections.

4.4.1.   Clay Calibration Improvement

The improvement provided by the clay calibration was measured by calculating the average
deviation with and without the coefficient of calibration applied. The gain of accuracy for the
clay calibration was assessed. The average deviation without the coefficient of calibration applied
was 0.49% against 0.46% with the coefficient applied. Even though this difference was low,
some minor improvement was achieved because most of the measurements were improved by the
coefficient of calibration. Table 15 shows the improvements achieved with the new calibration.
The column "Delta" refers to the difference between the deviations calculated with and without
the coefficient of calibration applied.

Table 15: Standard Deviation with and without the Coefficient of Calibration Applied for Clay Calibration.

Standard Name	Soil	Actual Ca content (%)	Original Ca content (%)	Deviation (%)	Modified Ca content (%)	Deviation (%)	Delta (%)
1	OHC	0.09	0.26	0.17	0.11	0.03	0.15
2	OHC	0.34	0.55	0.21	0.41	0.07	0.14
3	OHC	0.59	0.80	0.21	0.67	0.08	0.13
4	OHC	1.11	1.32	0.21	1.21	0.10	0.11
5	OHC	2.17	2.03	0.15	1.93	0.24	-0.09
6	OHC	3.60	3.52	0.08	3.47	0.13	-0.05
10	OHC	0.32	0.51	0.19	0.37	0.05	0.14
11	OHC	0.56	0.73	0.17	0.59	0.04	0.13
12	OHC	0.98	1.12	0.14	1.00	0.02	0.12
13	OHC	1.87	1.87	0.00	1.77	0.10	-0.10
14	OHC	3.66	4.31	0.65	4.28	0.62	0.03
15	OHC	0.46	0.60	0.15	0.47	0.01	0.14
16	OHC	0.74	0.82	0.07	0.69	0.06	0.02
17	OHC	1.39	1.31	0.08	1.19	0.20	-0.12
18	OHC	2.09	1.91	0.17	1.82	0.27	-0.10
19	OHC	5.95	4.27	1.69	4.24	1.71	-0.03
20	OHC	8.87	6.97	1.90	7.02	1.85	0.05
21	OHC	0.26	0.43	0.18	0.29	0.04	0.14
22	OHC	0.44	0.60	0.16	0.46	0.02	0.14
23	OHC	0.99	1.03	0.03	0.90	0.09	-0.06
24	OHC	1.91	1.93	0.02	1.84	0.08	-0.06
25	OHC	2.87	2.75	0.12	2.68	0.19	-0.07
26	OHC	7.58	6.75	0.83	6.79	0.79	0.04
27	OHC	11.08	9.77	1.31	9.90	1.18	0.13
28	SGB	1.39	1.31	0.08	1.19	0.19	-0.12
29	SGB	1.61	1.96	0.35	1.86	0.26	0.10
30	SGB	1.84	2.12	0.28	2.03	0.19	0.09
31	SGB	2.41	2.65	0.24	2.58	0.16	0.08
32	SGB	3.18	3.56	0.38	3.51	0.33	0.05
33	SGB	4.41	4.71	0.29	4.69	0.28	0.02
37	SGB	1.52	1.67	0.14	1.56	0.04	0.10
38	SGB	1.70	1.87	0.17	1.77	0.07	0.10
39	SGB	2.11	2.35	0.25	2.27	0.16	0.08
40	SGB	2.91	3.43	0.53	3.38	0.48	0.05
41	SGB	4.54	5.37	0.82	5.37	0.83	0.00
42	SGB	1.69	1.76	0.07	1.66	0.03	0.03

Table 15: Standard Deviation with and without the Coefficient of Calibration Applied for Clay Calibration (Continued)

Standard Name	Soil	Actual Ca content (%)	Original Ca content (%)	Deviation (%)	Modified Ca content (%)	Deviation (%)	Delta (%)
43	SGB	1.94	2.20	0.25	2.11	0.17	0.09
44	SGB	2.54	2.86	0.32	2.79	0.25	0.07
45	SGB	3.18	3.52	0.34	3.47	0.29	0.05
46	SGB	6.08	6.77	0.70	6.82	0.74	-0.05
47	SGB	9.12	10.11	0.99	10.25	1.13	-0.14
48	SGB	1.61	1.78	0.17	1.68	0.07	0.10
49	SGB	1.71	2.15	0.44	2.06	0.35	0.09
50	SGB	2.19	2.23	0.04	2.14	0.05	-0.01
51	SGB	2.96	3.93	0.97	3.89	0.93	0.04
52	SGB	3.86	4.13	0.26	4.10	0.23	0.03
53	SGB	7.86	7.52	0.34	7.58	0.28	0.06
54	SGB	11.36	10.62	0.74	10.78	0.58	0.16
			Average	0.38	Average	0.33	
			Std Dev	0.41	Std Dev	0.42	

Result of the linear regression, shown in Figure 16, demonstrates the improvement obtained by the calibration. The trend line related to modified measurements is closer to a y=x line than the trend line related to the raw measurements done during the clay calibration. However, a scatter for high Ca concentration (>5%) was observed which impacts the statistical analysis.

Figure 16: Ca Content Measurements Performed by S1 TITAN during the Clay Calibration with and without the coefficient of calibration applied

4.4.2. Summary of Findings from Clay Calibration Exercise

Some improvement in Ca measurement accuracy was provided by the calibration for clay samples. The average deviation and the linear regression analysis demonstrated that improvement. Generally, the improvement observed using the new calibration was low compared to the existing calibration that comes with PHXRF device. Moreover, some scattering was observed for samples with a high Ca content which probably come from the combination of OHC and SGB samples in a single calibration. As discussed before, OHC sample measurements are significantly further from actual values than SGB sample measurements for high Ca content samples. That is the most probable explanation for the scatter observed in Figure 16 for high Ca content during the clay calibration. Regrouping soils by specific parameters, such as mineralogy,

depositional environment, or particle size, in some specific calibration could reduce the scatter observed in Figure 16.

4.5. Sand Calibration

Sand calibration refers to the calibration done with SS samples only. Therefore, 19 samples were used for this calibration. The improvement provided by this calibration is discussed in the following sections.

4.5.1.   Sand Calibration Improvement

The improvement provided by the sand calibration was assessed using a procedure similar to that used for the clay calibration. The average of deviations with and without the coefficient of calibration applied were calculated. The sand calibration improvement was assessed by comparing those deviations. The average deviation of the Ca content measurements performed with the PHXRF without the coefficient applied is 0.46% against 0.53% with the coefficient applied. That improvement is more significant than the one for clay calibration and most of the measurement were improved by the calibration. As seen in Table 16 no relation between the Ca concentration and the improvement provided by the calibration can be observed. That is, the improvement provided by the calibration is the same for high and low Ca concentration.

Table 16: Standard Deviation with and without the Coefficient of Calibration Applied Comparison for Sand Calibration

Standard Name	Soil	Actual Ca content (%)	Original Ca content (%)	Deviation (%)	Modified Ca content (%)	Deviation (%)	Delta (%)
55	SS	0.07	0.14	0.07	-0.42	0.49	-0.42
56	SS	0.29	0.53	0.24	0.01	0.28	-0.04
57	SS	0.49	0.78	0.29	0.30	0.19	0.10
58	SS	0.93	1.59	0.66	1.19	0.26	0.41
59	SS	1.77	2.81	1.04	2.53	0.76	0.28
60	SS	3.39	4.71	1.32	4.62	1.23	0.09
61	SS	0.39	0.50	0.11	-0.02	0.41	-0.30
62	SS	0.70	0.97	0.27	0.50	0.20	0.07
63	SS	1.31	1.65	0.34	1.25	0.06	0.29
64	SS	1.98	2.05	0.07	1.69	0.29	-0.21
65	SS	4.86	5.54	0.68	5.54	0.68	0.00
66	SS	7.36	6.44	0.92	6.54	0.82	0.09
67	SS	0.24	0.43	0.19	-0.09	0.33	-0.14
68	SS	0.41	0.66	0.25	0.16	0.25	0.00
69	SS	0.93	1.39	0.46	0.96	0.03	0.43
70	SS	1.79	2.48	0.69	2.17	0.38	0.31
71	SS	2.64	3.65	1.01	3.46	0.82	0.19
72	SS	7.89	7.87	0.02	8.11	0.22	-0.20
73	SS	11.68	10.15	1.53	10.62	1.06	0.47
			Average	0.53	Average	0.46	
			Std Dev	0.45	Std Dev	0.34	

The linear regression results shown in Figure 17 also demonstrate the improvement achieved with the new calibration. The trend line related to modified measurements is closer to the y=x line than the trend line related to the raw measurements obtained during the sand calibration.
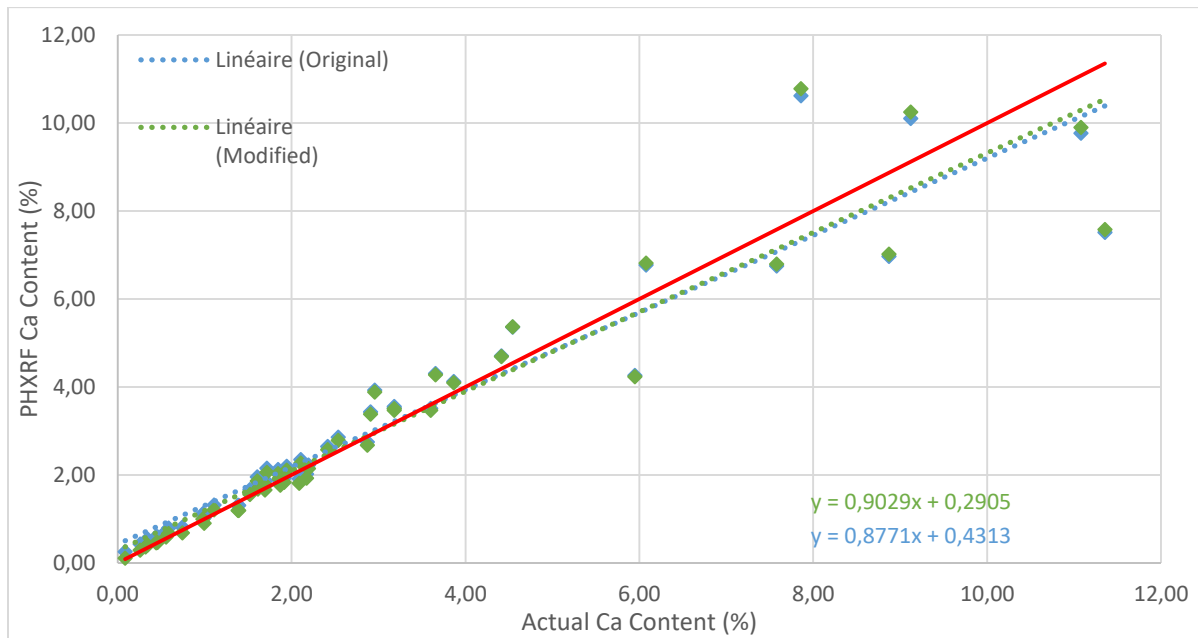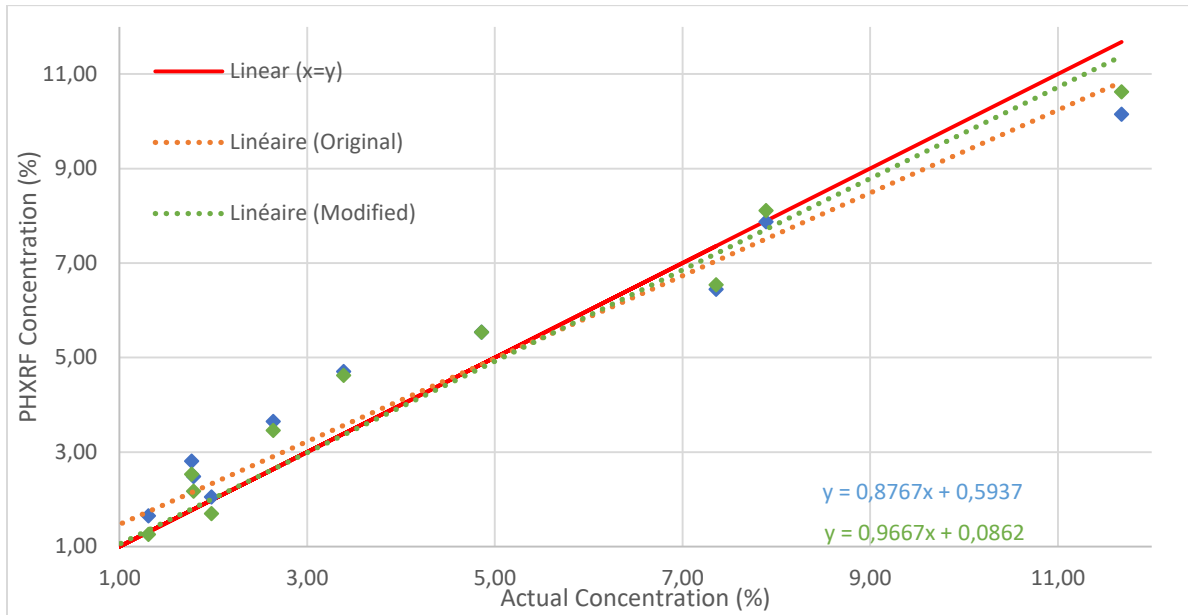
Figure 17: Ca Content Measurements Performed by S1 TITAN during the Sand Calibration with and without the coefficient of calibration applied

4.5.2. Summary of Findings from Sand Calibration Exercise

The improvement provided by the calibration for sand samples was also assessed. The comparison of average deviation and the linear regression analysis both showed that the calibration marginally improved the results. The improvement for sand samples is more significant than for clay samples because the PHXRF was less accurate for Ca content measurement during the calibration. This suggests that Ca content measurements performed by the S1 TITAN are not accurate using its original standard library configuration for sand samples. Even though some improvement was obtained using the new calibration, Table 15 shows some deviations higher than 1%. Those deviations are large compared to the clay calibration, where all deviations were lower than 0.5% when the coefficient of calibration was applied. That difference can be related to the sand grain size which is larger than the clay grain size. Big particles probably diffract the reflected X-ray emissions. This diffraction can impact the sample response

to the X-ray emission and consequently affect the results. That is one possible reason explaining this difference. However, this explanation is a theory and needs further research to be validated.

4.6. Validation

In this research, the goal of the validation phase was to assess the veracity of the conclusions made during the calibration procedure. The two calibrations, clay and sand, were input in the S1 TITAN and tested on several samples with a known CaO content. The samples were chosen to represent a wide range of concentration for each type of additive. The CaO content of samples was measured using the new calibrations and two other calibrations already present in the device. Those two manufacturer standard calibrations were also used to measure CaO content in untreated soil samples and additives. Three measurements of CaO content were performed for each sample for each method used. The samples were rotated on the device between each measurement to have an average CaO content present in the whole volume of the samples. The average of the three measurements were calculated and compared to the actual CaO content provided by Whole Rock XRF done by the independent laboratory ALS Global Geochemistry. The improvement of the calibration was deduced by comparing the difference and the standard deviation between the average measurements and the actual values. Improvement would be assessed by more accurate measurements using the new calibration. In the results presented below, the new calibration is referred to as "SC Cali" and the two others are referred as "Limestone" and "Geochem". The Limestone calibration is used for the detection of calcite for mining purposes and the Geochem one is a manufacturer standard for non-uniform or geological materials, also for mining purposes. Both OHC samples and SGB samples were tested during the

58

clay validation. The following sections present the results and conclusions about the validation

procedure.

4.6.1.   Validation with OHC Samples

The validation using OHC samples included eight different samples, two samples for each type of

additive used for this research (hydrated lime, CKD, fly ash and Portland cement). Table 17

shows the measurements performed with the PHXRF for the validation of OHC samples. Values

present in Table 17 are the averages of three independent measurements performed using the S1

TITAN.

Table 17: Average CaO Content Measurements Using Three Different Calibrations for OHC
Samples

	Limestone (%)	Geochem (%)	SC Cali (%)	Actual (%)
T3 (HL)	0.87	1.12	0.89	0.82
T6 (HL)	3.83	5.33	4.87	5.04
T12 (PC)	1.09	1.68	1.38	1.37
T14 (PC)	4.82	6.18	6.17	5.12
T16 (CKD)	0.79	1.25	0.90	1.04
T18 (CKD)	1.82	2.86	2.48	2.92
T24 (FA)	1.94	2.87	2.50	2.68
T27 (FA)	10.96	14.76	13.84	15.51
Raw OHC	0.27	0.29	0.11	0.12
Raw HL	52.91	73.48	75.65	71.85
Raw PC	44.33	50.13	50.33	63.56
Raw CKD	37.76	40.78	39.32	44.75
Raw FA	21.23	25.64	25.23	25.81

Using those averages of CaO content, stabilizer content was calculated for each sample tested

using Equation (1). As seen in Table 18, the new calibration is more accurate than only one of the

other calibrations. The average difference is 1.86% for Limestone against 0.97% for Geochem

and 1.27% for SC Cali. However, if the last samples (T27) is taken out of the average deviation

calculation, the new calibration becomes more accurate than both of the other calibrations. T27 is

the OHC sample mixed with 60% of fly ash. This percentage of fly ash is far outside the

recommendations present in OHD L-50, therefore it is reasonable to say that the clay calibration

is effective for field conditions as long as the recommendations are generally respected.

Table 18: Stabilizer Content Measured and Compared to the Actual Stabilizer Content Using Three Different Calibrations for OHC Samples

	Limestone (%)	Geochem (%)	SC Cali (%)	Actual SC (%)	Delta Limestone	Delta Geochem	Delta SC Cali
T3 (HL)	1.14	1.13	1.02	0.98	0.17	0.16	0.05
T6 (HL)	6.76	6.89	6.30	6.86	0.10	0.03	0.56
T12 (PC)	1.86	2.78	2.52	1.97	0.11	0.81	0.55
T14 (PC)	10.33	11.83	12.06	7.88	2.45	3.94	4.18
T16 (CKD)	1.38	2.37	2.01	2.06	0.68	0.31	0.05
T18 (CKD)	4.14	6.35	6.04	6.27	2.14	0.08	0.23
T24 (FA)	7.96	10.18	9.53	9.96	2.00	0.21	0.44
T27 (FA)	51.01	57.10	54.67	59.91	8.90	2.81	5.24
B (HL)	3.21	3.40	3.13	3.00	0.21	0.40	0.13
				Average Delta	1.86	0.97	1.27
				Std Dev	2.81	1.41	1.98

SC values presented in Table 18 were calculated using raw soil, raw additive and mixed soil CaO

measurements performed by the device. Even though the additives were not included in the

calibrations process as standard samples, their CaO contents were measured for the SC

calculation during the validation. However, Table 17 shows that measured CaO contents for

additives using the new calibration can be far from the actual values. Therefore, SC was also

calculated using the actual values of CaO content measured by ALS Geochemistry to compare

the accuracy changes. For the same reason, SC was also calculated using actual CaO values of the

additives and the raw soil. These comparisons were done to determine what part of the difference

between actual and measured SC values come from the measurements of the mixed samples,

which is the part primarily addressed by the calibration. As seen in Table 19, using the actual

CaO content of the additives and raw soil improved the accuracy of the PHXRF. SC Cali/1 refers

to the SC calculated with actual additive and raw soil CaO content. SC Cali/2 refers to the SC

calculated with only actual additive CaO content. SC Cali/3 refers to the SC calculated with all

values determined by PHXRF measurements of additive, raw soil and mixed soil.

Table 19: Comparison Between Three Different Calculation of Stabilizer Content for the same OHC Samples

	SC Cali/1 (%)	SC Cali/2 (%)	SC Cali/3 (%)	Actual SC (%)	Delta SC Cali/1	Delta SC Cali/2	Delta SC Cali/3
T3 (HL)	1.07	1.08	1.02	0.98	0.09	0.10	0.05
T6 (HL)	6.62	6.63	6.30	6.86	0.24	0.23	0.56
T12 (PC)	1.98	1.99	2.52	1.97	0.01	0.02	0.55
T14 (PC)	9.54	9.55	12.06	7.88	1.66	1.67	4.18
T16 (CKD)	1.75	1.77	2.01	2.06	0.31	0.30	0.05
T18 (CKD)	5.29	5.31	6.04	6.27	0.98	0.97	0.23
T24 (FA)	9.28	9.31	9.53	9.96	0.68	0.65	0.44
T27 (FA)	53.42	53.43	54.67	59.91	6.49	6.48	5.24
B (HL)	3.29	3.30	3.13	3.00	0.29	0.30	0.13
				Average Delta	1.19	1.19	1.27
				Std Dev	2.05	2.05	1.98

The average difference between the three calculation methods is low for OHC validation. The

fact that the clay calibration gave good result with the raw soil and mixed soil measurement

explains the non-significant difference. However, as shown in a subsequent section, significant

differences were obtained for the sand calibration.

4.6.2. Validation with SGB Samples

Two samples for each additive type were used for the validation of SGB samples. Table 20 presents the CaO measurements performed with the PHXRF for the validation of SGB samples. Values presented in Table 20 are the averages of three independent measurements performed using the S1 TITAN.

Table 20: Average CaO Content Measurements Using Three Different Calibrations for SGB Samples

	Limestone (%)	Geochem (%)	SC Cali (%)	Actual (%)
T30 (HL)	2.63	3.38	2.80	2.58
T33 (HL)	5.93	7.39	6.61	6.18
T39 (PC)	3.01	3.54	3.15	2.95
T41 (PC)	6.41	7.71	7.52	6.36
T42 (CKD)	2.08	2.60	2.24	2.37
T47 (CKD)	13.32	14.82	14.18	12.77
T49 (FA)	2.59	2.90	2.65	2.40
T52 (FA)	4.81	6.21	5.66	5.41
Raw SGB	1.60	1.85	1.54	1.94
Raw HL	52.91	73.48	75.65	71.85
Raw PC	44.33	50.13	58.21	63.56
Raw CKD	37.76	40.78	39.32	44.75
Raw FA	21.23	25.64	25.23	25.81

As seen in Table 21, "SC Cali" method was slightly more accurate than both "Limestone" and "Geochem". The average delta obtained using the new calibration is lower than the ones using the two other calibrations. Indeed, the average deviation using the new calibration is 2.60% against 2.69% for Limestone and 3.13% for Geochem. Therefore, some small improvement was obtained, and the new calibration was validated for SGB samples. However, the average difference is twice larger than the one for OHC validation, so the accuracy of the HPXRF for SC measurements varies for different types of clay.

Table 21: Stabilizer Content Measured and Compared to the Actual Stabilizer Content Using Three Different Calibrations for SGB Samples

	Limestone (%)	Geochem (%)	SC Cali (%)	Actual SC (%)	Delta Limestone	Delta Geochem	Delta SC Cali
T30 (HL)	2.00	2.14	1.70	0.92	1.08	1.22	0.78
T33 (HL)	8.44	7.75	6.84	6.06	2.37	1.68	0.78
T39 (PC)	3.30	3.52	3.31	1.64	1.66	1.88	1.21
T41 (PC)	11.25	12.14	12.26	7.17	4.08	4.97	3.38
T42 (CKD)	1.31	1.93	1.85	1.00	0.31	0.93	0.85
T47 (CKD)	32.42	33.31	33.47	25.30	7.12	8.01	8.17
T49 (FA)	5.01	4.43	4.71	1.93	3.08	2.50	2.78
T52 (FA)	16.35	18.35	17.39	14.54	1.82	3.81	2.85
				Average Delta	2.69	3.13	2.60
				Std Dev	2.13	2.40	2.49

As with OHC samples, SC was also calculated using actual CaO content of additives, and another time using actual additive and raw soil CaO content. As seen in Table 22, using the actual CaO content of the additives and raw soil improved the accuracy of the PHXRF compared to the two other calculation methods. SC Cali/1 refers to the SC calculated with actual additive and raw soil CaO content. SC Cali/2 refers to the SC calculated with only actual additive CaO content. SC Cali/3 refers to the SC calculated with PHXRF measured values of additive, raw soil and mixed soil.

Table 22: Comparison Between Three Different Calculation of Stabilizer Content for the same SGB Samples

	SC Cali/1 (%)	SC Cali/2 (%)	SC Cali/3 (%)	Actual SC (%)	Delta SC Cali/1	Delta SC Cali/2	Delta SC Cali/3
T30 (HL)	1.23	1.79	1.70	0.92	0.31	0.88	0.78
T33 (HL)	6.68	7.21	6.84	6.06	0.61	1.15	0.78
T39 (PC)	1.97	2.60	2.85	1.64	0.33	0.96	1.21
T41 (PC)	9.05	9.64	10.55	7.17	1.88	2.47	3.38
T42 (CKD)	0.70	1.62	1.85	1.00	0.31	0.61	0.85
T47 (CKD)	28.60	29.26	33.47	25.30	3.30	3.96	8.17
T49 (FA)	2.99	4.59	4.71	1.93	1.06	2.67	2.78
T52 (FA)	15.57	16.97	17.39	14.54	1.04	2.43	2.85
				Average Delta	1.11	1.89	2.60
				Std Dev	1.04	1.17	2.49

The improvement provided using actual CaO content of raw soil and additives for the SC calculations is significant as the average difference using actual CaO content of additives and raw soils is half the one using measured values. That suggests that the clay calibration is not appropriate to measure CaO content in raw soil and additives as seen in Table 23.

Table 23: Average CaO Content Measurements Using Three Different Calibrations for Raw Soil and Additive

	Limestone (%)	Geochem (%)	SC Cali (%)	Actual (%)
Raw SGB	1.60	1.85	1.54	1.94
Raw HL	52.91	73.48	75.65	71.85
Raw PC	44.33	50.13	58.21	63.56
Raw CKD	37.76	40.78	39.32	44.75
Raw FA	21.23	25.64	25.23	25.81

Results in Table 21 would suggest that another calibration is possibly needed for SGB soil alone, because the average difference is twice the one for OHC samples. However, Table 19 and Table 22 shows that the average difference of OHC and SGB samples are similar using actual CaO

content of raw soil and raw additives. This would suggest that the clay calibration may be appropriate for different types of clay provided accurate values of CaO content in the additive could be determined. It seems feasible in the case of actual construction projects to obtain additive samples, and possibly raw soil samples, in advance of construction to allow time for testing using the XRF Whole Rock method.

4.6.3. Validation with Sand Samples

No sand sample was mixed with hydrated lime because lime does not react with sand. Therefore, only 6 samples were used for the validation of sand samples, two composed of Portland cement, two composed of CKD and two composed of fly ash. Table 24 shows the measurements performed with the PHXRF for the validation of SS samples. Values presented in Table 24 are the averages of three independent measurements performed using the S1 TITAN.

Table 24: CaO Content Measurements Using Three Different Calibrations for SS Samples

	Limestone	Geochem	SC Cali	Actual
T57 (PC)	5.76	4.65	6.87	0.69
T60 (PC)	7.82	10.17	6.56	4.75
T62 (CKD)	1.63	2.02	0.81	0.98
T66 (CKD)	15.65	14.81	10.45	10.30
T71 (FA)	5.16	7.67	4.83	3.70
T73 (FA)	16.35	20.75	13.92	16.34
Raw SS	0.40	0.37	0.49	0.10
Raw PC	44.33	50.13	36.77	63.56
Raw CKD	37.76	40.78	29.41	44.75
Raw FA	21.23	25.64	18.81	25.81

As seen in Table 25, "SC Cali" method was more accurate than both "Limestone" and "Geochem" methods. The average difference obtained using the new calibration is much lower

than the ones using the two other calibrations. Therefore, some improvement was obtained, and the new calibration was validated for SS samples.

Table 25: Stabilizer Content Measured and Compared to the Actual Stabilizer Content Using Three Different Calibrations for SS Samples

	Limestone (%)	Geochem (%)	SC Cali (%)	Actual SC (%)	Delta Limestone	Delta Geochem	Delta SC Cali
T57 (PC)	12.19	8.60	17.60	0.93	11.26	7.67	16.67
T60 (PC)	16.90	19.69	16.72	7.33	9.57	12.36	9.40
T62 (CKD)	3.28	4.09	1.10	1.97	1.31	2.12	0.87
T66 (CKD)	40.80	35.74	27.46	22.84	17.96	12.89	4.61
T71 (FA)	22.82	28.87	23.71	14.00	8.82	14.87	9.71
T73 (FA)	76.56	80.64	73.31	63.17	13.39	17.47	10.15
T(CKD)	14.39	15.94	14.63	9.00	5.39	6.94	5.63
				Average Delta	9.67	10.62	8.15
				Std Dev	5.38	5.29	5.04

However, the average difference between measured and actual values is much larger than the one obtained for OHC and SGB validation. Therefore, the validation agrees with the observation discussed in Section 4.5 about the difference of accuracy of the PHXRF for SC measurements between clay and sand samples.

The difference between actual and measured Ca content for additives and raw soil is much greater using sand calibration. Therefore, as with the clay soils, SC was also calculated using actual additive CaO value, and using actual additive and raw soil CaO values. In Table 26, SC Cali/1 refers to the SC calculated with actual additive and raw soil CaO content. SC Cali/2 refers to the SC calculated with only actual additive CaO content. SC Cali/3 refers to the SC calculated with PHXRF measured values of additive, raw soil and mixed soil. As seen in Table 26, using the actual CaO content of the additives and raw soil greatly improved the accuracy of the PHXRF

calculations of SC. However, using only actual CaO values of additives improved this accuracy

slightly more than using both raw soil and additive actual CaO content.

Table 26: Comparison Between Three Different Calculation of Stabilizer Content for the same SS Samples

	SC Cali/1 (%)	SC Cali/2 (%)	SC Cali/3 (%)	Actual SC (%)	Delta SC Cali/1	Delta SC Cali/2	Delta SC Cali/3
T57 (PC)	10.68	10.12	17.60	0.93	9.75	9.19	16.67
T60 (PC)	10.18	9.62	16.72	7.33	2.85	2.29	9.40
T62 (CKD)	1.58	0.72	1.10	1.97	0.39	1.25	0.87
T66 (CKD)	23.18	22.51	27.46	22.84	0.34	0.34	4.61
T71 (FA)	18.40	17.15	23.71	14.00	4.40	3.15	9.71
T73 (FA)	53.74	53.03	73.31	63.17	9.42	10.13	10.15
T(CKD)	10.35	9.56	14.63	9.00	1.35	0.56	5.63
				Average Delta	4.07	3.85	8.15
				Std Dev	4.03	4.10	5.04

The improvement provided using actual CaO content of raw soil and additives for the SC

calculations is significant, as the average difference using actual CaO content of additives and

raw soils is half the one using PHXRF measured values. As with the clay validation exercise, this

suggests that the sand calibration is not appropriate to measure CaO content in the additives and

accuracy of calculated SC content could be improved in real projects by obtaining additives and

possibly soil samples in advance of construction for Whole Rock XRF testing.

4.6.4. Summary of the Findings from Validation Exercise

The validation process showed that clay calibration is reasonably accurate for OHC samples but

does not provide any significant improvement compared to existing calibrations that come with

the PHXRF. However, the combined OHC/SGB clay calibration slightly improved the accuracy

of the PHXRF for SGB samples compared to the other calibrations. Nevertheless, a significant

difference between OHC and SGB validation results was observed as the average SC difference

was twice larger for SGB samples. However, other SC calculations using actual CaO content of

additives and raw soils demonstrated that the differences were primarily due to the inaccuracy of

CaO content of additives determined by the PHXRF and possibly to some extent inaccuracy of

the CaO content of raw soils as measured with the PHXRF. Raw soils and additives were not

included in the clay calibration which may account to some extent why the PHXRF cannot

measure accurately the CaO of these parameters. Additionally, using Equation (1), the PHXRF

measurement errors are compounded since they are present in each of the three CaO

measurements used to calculate SC. Using actual raw soil and additive CaO contents obtained by

Whole Rock XRF in combination with PHXRF measurements on treated soils greatly improves

the accuracy of the calculated SC. The improvement is most attributed to using the actual CaO

content of the additive. Practically, is should be a rather simple task to obtain samples of additive,

and possibly raw soil, in advance of construction for Whole Rock XRF testing. In this way the

accuracy of SC determined by PHXRF measurements using Equation (1) or Equation (4) could

be greatly improved with relatively little additional effort.

A significant difference between sand and clay calibration was observed even using actual CaO

content of raw soils and additives. The most probable explanation is that size of constituent

particles influences the accuracy of the PHXRF measurements. Ferraro (2016) showed that

processing over a finer sieve leads to more accurate PHXRF measurements. It seems that the size

of the particle grains, including individual grains within aggregated clumps that pass through the

sieve openings, may also have an impact on the device accuracy. For example, individual sand

grains for the sand used in this study were visible and many particles were of a size not much

smaller than the No. 40 sieve openings (0.425 mm). However, the clay particles are microscopic

and known to be less than about 1 or 2 microns in size.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The purpose of this research was to create a new calibration specifically related to chemical stabilizers in soils for a PHXRF device to improve the measurement of SC for quality control and forensic investigations. This was achieved by creating some samples with a wide range of SC using different combinations of soils and additives. These samples were used as standard samples for the new calibration. A global calibration, including every standard sample, was created first. The global calibration did not improve the Ca content measurements provided by the PHXRF with its standard internal calibration. However, a relationship between the type of soil and the device accuracy for Ca measurement was observed during the global calibration. Therefore, two other calibrations were created; one using only clay samples (OHC and SGB samples) and another using only sand samples (SS samples). The improvement provided by these two new calibrations was demonstrated as the accuracy of the PHXRF for Ca content measurements was improved with the new coefficients of calibration applied. This improvement was validated on samples not used in the calibration, and it was observed that SC values measured for some samples were closer to actual SC values using the new calibrations than two other existing calibrations intrinsic to the device.

It has been demonstrated that the new calibrations did not perform well in detecting CaO content of raw additives. Indeed, the CaO measurements performed using PHXRF on raw additives and the new calibrations were significantly far from the actual values provided by ALS

Geochemistry. The fact that the additive samples were not part of the standard samples for the calibrations helps explain this difference between the measured and the actual values of CaO in additives. It was also noted that significant improvements in the calculated SC values were obtained when actual values of CaO in the additive were used in combination with PHXRF measurements of CaO in the stabilized samples. And improvements were even marginally better when actual values of CaO in the raw soils and additive were included with PHXRF measurements on the stabilized soil in calculating SC content.

A significant accuracy gap for SC measurements was observed between clay and sand samples. The accuracy for sand samples was less than that for clay samples. A possible explanation for this difference is that sand particles are larger than clay particles and consequently have a greater impact on the diffraction of X-ray emissions that adversely impacts the measurements.

5.2. Recommendation for Future Research

As seen in the validation section (Section 4.6), the PHXRF has a different accuracy for SC measurement for each soil and additive type. That is, each combination of a specific soil mixed with a specific additive can present significant differences in SC measurement. Therefore, a specific calibration related to a specific combination should be created for every possible combination to fill this gap of accuracy in the PHXRF. If these calibrations are created, the user may be able to measure SC content for every field situation with a good accuracy.

Some research about the accuracy of the calibrations made during this research needs to be conducted under field conditions. Field conditions may differ from the conditions of the standard samples used for the calibrations. Such research will clarify the influence of moisture content on

the accuracy of the PHXRF and define field requirements for the new calibrations. The goal of that research would be to confirm the usability of the new calibrations under actual field conditions and to create some specifications regarding the use of those calibrations in the field.

Some research investigating the scatter observed for high Ca content during the clay calibration is needed. Such research will improve the accuracy of the clay calibration and the determination of SC in soil subgrades. The new PHXRF calibrations created are inappropriate for measuring CaO content in additives. Therefore, additional research needs to focus on improving these measurements to have more accurate SC measurements. Possible research could focus on the creation of a separate calibration specific to CaO content in chemical stabilizers. Thus, the user would have an appropriate calibration to perform accurate measurements of CaO content of additives.

The difference of accuracy between clay samples and sand samples also needs to be investigated. A possible reason explaining this gap in accuracy was exposed in this research, but investigations need to be conducted to verify this hypothesis. Size of sand particles, which are larger than clay particles, is assumed to be the reason for the accuracy gap in this research. Therefore, testing some sand pulverized to a finer state could verify that hypothesis.

Sulfates in soil is also an important element that needs to be measured accurately. Therefore, some research, similar to the one described in this paper, but focused on sulfate determination are recommended. Swell problems induced by sulfate concentrations in soils are a common problems in areas where subgrade stabilization is used. Using X-ray fluorescence to detect sulfates in soils could improve investigations and improve the management of swelling problems induced by sulfates in treated subgrades.

REFERENCES

Alberghina, Barraco, Brai, Pellegrino, Schiavone, and Tranchina, "Gilding and Pigments of Renaissance Marble of Abatellis Palace: Non-Invasive Investigation by XRF Spectrometry," <u>X-Ray Spectrometry,</u> Vol. 42, No. 2, March 2013.

Artamonova, "SR-XRF Analysis and Assessment in Urban Ecology Studies: The Case of Novosibirsk," <u>Journal of Surface Investigation. X-Ray, Synchrotron and Neutron Techniques,</u> Vol.5, No. 6, December 2011, pp. 1085-1090.

Bernick, Kalnicky, Prince, and Singhvi, "Results of Field-Portable X-Ray Fluorescence Analysis of Metal Contaminants in Soil and Sediment," <u>Journal of Hazardous Material,</u> Vol. 43, February 1995, pp. 101-110.

Cerato, and Miller, "Determination of Soil Stabilizer Content Using X-Ray Fluorescence," <u>Geotechnical Testing Journal</u>, Vol. 36, No. 5, 2013.

Cocka, "Use of Class C Fly Ashes for the Stabilization of an Expensive Soil," <u>Journal of Geotechnical and Geoenvironmental Engineering</u>, Vol. 7, No. 127, 2001, pp. 568-573.

Gerward, "The Dawn of X-Ray Spectroscopy," <u>X-Ray Spectroscopy,</u> Vol. 42, No. 5, September 2013, pp. 343-348.

Miller, and Zaman, "Field and Laboratory Evaluation of Cement Kiln Dust as a Soil Stabilizer," <u>Transportation Research Record</u>, Vol. 1714, No. 00-0869, 2000, pp. 25-32.

Moseley, "The High-Frequency Spectra of the Elements," <u>The Philosopher Magazine,</u> Vol. 26, 1913, pp. 1024-1034

Nuevo, and Martin Sanchez, "Application of XRF Spectrometry to the Study of Pigments in Glazed Ceramic Pots," <u>Applied Radiation and Isotopes</u>, Vol. 69, No. 3, 2011, pp. 574-579.

Parmar, and Singh, "Elemental Analysis of Chelant Induced Phytoextraction by 'Pteris Vittata' Using WD-XRF Spectrometry," <u>International Journal of Agriculture,</u> Vol. 9, No. 1, Feb 2016, pp.107-115.

Parsons, Grabulosa, Pili, Floor, Roman-Ross, and Charlet, "Quantification of Trace Arsenic in Soils by Field-Portable X-ray Fluorescence Spectrometry: Considerations for Sample Preparation and Measurement Conditions," <u>Journal of Hazardous Material,</u> Vol. 262, November 2013, pp. 1213-1222.

Juan D. Pinilla, Gerald A. Miller, Amy B. Cerato, and Donald S. Snethen, "Influence of Curing Time on the Resilient Modulus of Chemically Stabilized Soils," <u>Geotechnical Testing Journal,</u> Vol. 34, No. 4, 2011.

Ranjan K. Rout, Pinit Ruttanaporkmakul, Shashank Valluru, Anand J. Puppala, "Resilient Modulus of Lime-Cement Treated Subgrade Soils," <u>GeoCongress</u>, ASCE 2012, Department of Civil Engineering, Houstan, Texas.

Reddy, Attaelmanan, and Mouton, "Pots, Plates and Provenance: Sourcing Indian Coarse Wares from Mleiha Using X-Ray Fluorescence (XRF) Spectrometry Analysis," <u>IOP Conference Series: Materials Science and Engineering</u>, Vol. 37, No. 1, 2012.

Rouillon, and Taylor, "Can field portable X-ray fluorescence (pXRF) produce high quality data for application in environmental contamination research ?," <u>Environmental Pollution,</u> Vol. 214, July 2016, pp. 255-264.

Saleh-E-In, Sultana, Hossain, Ahsan, and Roy, "Elemental Analysis of Anethum Sowa L. (Dill) Root by XRF Spectrometry," <u>Bangladesh Journal of Scientific and Industrial Research</u>, Vol. 46, No. 3, November 2011.