Distribution of Chloride, pH, Resistivity, and Sulfate Levels in Backfill for Mechanically-Stabilized Earth Walls and Implications for Corrosion Testing

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Disclaimer

Approximate Conversions to SI Units

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
LENGTH				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
AREA				
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
VOLUME				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
TEMPERATURE (exact degrees)				
°C	Celsius	1.8C+32	Fahrenheit	°F

*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.
(Revised March 2003)
(Downloaded from http://www.fhwa.dot.gov/aaa/metricp.cfm January 2015)

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16. Abstract

The ultimate goals of this research were to improve quality, speed completion, and reduce risk in mechanically-stabilized earth (MSE) wall projects. Research objectives were to assure (1) that variability in the corrosion properties of soil (pH, minimum resistivity, chloride, and sulfate levels) due to sampling and analytical technique was much lower than variability in these levels within and between soil sources and types and thus did not inflate the risk of emplacing a corrosive soil as MSE wall backfill, (2) that the number of soil type samples analyzed prior to acceptance of a backfill was appropriate, based on the expected distribution of corrosion properties within the backfill, and (3) that the corrosion properties of backfill material did not change appreciably over time, especially after emplacement and over the design lifetime of an MSE wall. Corrosion properties of soil were tested with Florida Methods (FMs) 5-550, 5-551, 5-552, and 5-553 for pH, minimum resistivity, water-soluble chloride, and water-soluble sulfate, respectively. Changes to the quality assurance (QA) plan for acceptance quality characteristics (AQC) of backfill corrosion properties were recommended based on research outcomes. These changes had as their focus an improvement in the buyer's statistical power to accept good backfill material through reductions in test error associated with material properties, sample processing, and laboratory procedures. Recommended changes included (1) proposed revisions to the FMs for pH, minimum resistivity, chloride, and sulfate, (2) an increase in the number of independent samples tested for pH and minimum resistivity, (3) a revised acceptance limit for minimum resistivity, (4) method operator training and independent audits, (5) an inter-laboratory study post-implementation of the revised methods, and (6) re-evaluation of the need for chloride and sulfate testing for backfill above a pre-determined minimum resistivity. Geochemical modeling with the U. S. Geological Survey (USGS) model PHREEQC for a conservative case of a low ionic strength and poorly buffered sandy backfill revealed that in a few years' time the pore water of emplaced backfill could equilibrate with infiltrating rainfall. The model results suggested that a soil's buffering capacity might be important consideration when metal is used as reinforcement in MSE wall backfill. Field and laboratory testing of candidate sands to calibrate the model were recommended ahead of any proposed changes to the QA plan based on model results.

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Executive Summary

The ultimate goals of this research were to improve quality, speed completion, and reduce risk in mechanically-stabilized earth (MSE) wall projects. Research objectives were (1) to assure that variability in the corrosion properties of soil (pH, minimum resistivity, chloride, and sulfate levels) due to sampling and analytical technique was much lower than variability in these levels within and between soil sources and types and thus did not inflate the risk of emplacing a corrosive soil as MSE wall backfill, (2) that the number of soil type samples analyzed prior to acceptance of a backfill was appropriate, based on the expected distribution of corrosion properties within the backfill, and (3) that the corrosion properties of backfill material did not change appreciably over time, especially after emplacement and over the design lifetime of an MSE wall. Corrosion properties of soil were tested with Florida Methods (FMs) 5-550, 5-551, 5-552, and 5-553 for pH, minimum resistivity, water-soluble chloride, and water-soluble sulfate, respectively.

Divergence in corrosion test results between laboratories was seen for pH, minimum resistivity, chloride, and sulfate for one or more of the eight sands collected from mines as part of this study. Changes to the FMs for minimum resistivity, chloride, and sulfate that were tested by USF showed promise for improving between-laboratory agreement. Split sample analyses revealed that four of the eight sands failed to meet an acceptance limit for one or more of the corrosion properties in one or more of the partnered laboratories. If the split sample analyses between two laboratories represented quality control and verification tests, at least three out of the eight sands would have required resolution testing. Reduction in a relatively high rate of resolution testing may offset additional costs associated with method improvements.

Replicate studies of mined soils for each corrosion FM produced an estimate of test error that included contributions from material properties, environmental influences, and sampling, processing, and single-operator testing (method repeatability) of soils. For each FM, its test error estimate was adjusted to include the contribution from multi-laboratory testing (method reproducibility). The adjusted estimate was incorporated into a method operating characteristic (OC) curve, which had a Type I (α) error of 0.01 and a Type II (β) error of 0.05; the OC curve related the buyer's statistical power ($1-\beta$) to accept a good backfill to the number of samples, test error, and acceptance limit(s).

Changes to the quality assurance (QA) plan for acceptance quality characteristics (AQC) of backfill corrosion properties were recommended based on research outcomes. These changes had as their focus an improvement in the buyer's statistical power to accept good backfill material through reductions in test error associated with material properties, sample processing, and laboratory procedures. Recommended changes included (1) proposed revisions to the FMs for pH, minimum resistivity, chloride, and sulfate, (2) an increase in the number of independent samples tested for pH and minimum resistivity, (3) a revised acceptance limit for minimum resistivity, (4) method operator training and independent audits, (5) an inter-laboratory study post-implementation of the

revised methods, and (6) re-evaluation of the need for chloride and sulfate testing for backfill above a pre-determined minimum resistivity. Recommended changes are outlined below:

- *Revise the FMs for pH, minimum resistivity, chloride, and sulfate.* Proposed revisions to the FMs included (1) minor edits to method grammar, organization, and units of measure, (2) updates to the apparatus and reagents sections, with a hazardous materials note as appropriate, (3) step-by-step instructions to facilitate method oversight, (4) one or more QA/QC procedures, and (5) a new section for method precision and bias.

- *Increase the number of independent samples per soil type for pH and minimum resistivity.* Recommended for pH were at least three independent pH samples per soil type tested both pre-construction and post-emplacement. Recommended for minimum resistivity were at least two minimum resistivity samples per soil type tested both pre-construction and post-emplacement and an increase in the acceptance limit to 4,000 ohm-cm.

- *Conduct operator training and routine on-site laboratory audits of the FMs*. Operator training was recommended for all FMs, for example, training through a video demonstration of each method as well as method outcomes for both well-executed and poorly-executed procedures. Also recommended for FMs were routine independent audits, which provide oversight on method performance and put the method and operator in a context that includes environmental influences (temperature, noise, dust, crowding), laboratory practices, and pressure for time.

- *Perform a Florida-wide inter-laboratory study of the revised FMs*. A Florida-wide inter-laboratory study of the revised FMs within a year of adoption was recommended to assure that FDOT and commercial laboratories were proficient with the revised methods and to establish for each FM the method reproducibility.

- *Re-evaluate the FMs for chloride and sulfate.* A review of Florida-wide post-revision chloride and sulfate results for MSE wall backfill after a two-year data collection period was recommended to assess if further testing of chloride and sulfate were necessary for select backfill above a pre-determined minimum resistivity.

Geochemical modeling with the U. S. Geological Survey (USGS) model PHREEQC for a conservative case of a low ionic strength and poorly buffered sandy (quartz) backfill revealed that in a few years' time the pore water of emplaced backfill could equilibrate with infiltrating rainfall. The model results suggested that a soil's buffering capacity might be an important consideration when metal is used as reinforcement in MSE wall backfill. Field and laboratory testing of candidate sands to calibrate the model were recommended ahead of any proposed changes to the QA plan based on model results.

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List of Abbreviations

200%	fraction of aggregate passing through a 200 mesh sieve
Ag/AgCl	silver/silver chloride
AASHTO	American Association of State Highway and Transportation Officials
ASTM	ASTM International, formerly the American Society for Testing and Materials
AQC	acceptance quality characteristic
C-22	sampling datasheet
C-S-H	calcium silicate hydrates
CEI	Construction Engineer and Inspector
cm	centimeter
CO_2	carbon dioxide
CR	corrosion rate
CV	coefficient of variation
D2S	maximum acceptable difference between test results
FDOT	Florida Department of Transportation
F-test	Used to test if variances from two populations are equal
F	Faraday’s constant (Equation 3-1)
FM	Florida Method
H^+, H_3O^+	hydronium, proton
hr	hr, hr
Hz	hertz
I	current
LL	liquid limit
LIMS	laboratory information management system
LOD	limit of detection
M	molar; moles/liter
MDL	minimum detection level
min	minute
MSE	mechanically-stabilized earth
N	number of samples
n	number of electrons participating in an electrochemical reaction (Equation 3-1)
NADP	National Atmospheric Deposition Program
NH_4^+	ammonium
NO_3^-	nitrate
NIST	National Institute for Standards and Technology
nm	nanometer
NTN	NADP National Trends Network
OC	operating characteristic
%OM	% organic matter
PHREEQC	pH redox equilibrium model coded in ‘C’
PI	plasticity index

ppm	parts per million
QA/QC	quality assurance/quality control
QST	Qualified Sampling Technician
R	gas constant (Equation 3-1)
R	surface recession (Equation 2-3)
R, R_T, $R_{15.5}$	resistance, resistance at observed temperature, resistance at 15.5 ^oC (Equation 3-4)
%RE	% relative error
%RSD	% relative standard deviation
s	sample standard deviation
s_r	repeatability standard deviation
s_R	reproducibility standard deviation
SMEWW	Standard Methods of Evaluation for Water and Wastewater Analysis
SMO	FDOT State Material Office
SO_2	sulfur dioxide
SO_4^{2-}	sulfate
t-test	Student’s t-test, use making inferences about the means for a small sample size
Type I (α)	false positive; incorrect rejection of the null hypothesis
Type II (β)	false negative, failure to reject a false hypothesis
USEPA	United States Environmental Protection Agency
USF	University of South Florida
USGS	United States Geological Survey
W/C	water to concrete ratio
V	volts
yr	year
μ	mean, average
$\mu g\ m^{-3}$	micrograms per cubic meter
μm	micrometer
σ	population standard deviation, test error
$\sqrt{\sigma_{total}^2}$	total test error
ρ	soil resistivity

1 Introduction

1.1 Research Statement

Construction of mechanically-stabilized earth (MSE) walls in metropolitan areas within FDOT's Districts 1 and 7 has put pressure on local mines for soil that meets the requirements for select backfill (material 092L). MSE walls are designed with reinforcement that consists of wire mesh, metal strips, or structural geosynthetics; such reinforcement is imbedded in select backfill. Select backfill must be non-corrosive, non-plastic, have a low liquid limit, and have low organic matter and fine particle content (Scheer, 2013). Acceptance testing of select backfill occurs after emplacement and compaction. The purpose of this research was to increase the probability that after emplacement and compaction the acceptance quality characteristics (AQC) for corrosion properties of select backfill were correctly met. Variability in measured corrosion properties was seen not only because of soil heterogeneity, but also because of sampling strategies and analytical methods. Improvements in sampling strategies and analytical methods were proposed with the intent to improve the decision to accept or reject a select backfill.

1.2 Scope and Objectives

The ultimate goals of this research were to improve quality, speed completion, and reduce risk of mechanically-stabilized earth (MSE) wall projects. Research objectives were to assure (1) that variability in the corrosion properties of soil (pH, minimum resistivity, chloride, and sulfate levels) due to sampling and analytical technique was much lower than variability in these levels within and between soil sources and types and thus did not inflate the risk of emplacing a corrosive soil as MSE wall backfill, (2) that the number of soil type samples analyzed prior to acceptance of a backfill was appropriate, based on the expected distribution of corrosion properties within the backfill, and (3) that the corrosion properties of backfill material did not change appreciably over time, especially after emplacement and over the design lifetime of the MSE wall. Corrosion properties of soil were tested with Florida Methods (FMs) 5-550, 5-551, 5-552, and 5-553 for pH, minimum resistivity, water-soluble chloride, and water-soluble sulfate, respectively.

The scope of this research included tasks to (1) review relevant literature, (2) examine trends in corrosion properties of Districts 1 and 7 MSE backfill mines based on existing data, (3) determine the single-laboratory contributions to method reproducibility of factors that relate to field sampling and laboratory analysis and improve method reproducibility through changes in the methods, (4) discover the distribution of corrosion properties within and between mines for a representative sample of mines as suggested by objective (2), (5) model analytically the potential for the corrosion properties of MSE backfill to change over time with an initial focus on changes due to the ionic composition of rainfall, (6) determine multi-laboratory contributions to method reproducibility, and (7) disseminate the project results as a final report. Tasks 1 through 6 are briefly described in the following sections. This research was limited to 10 soils that were candidate materials for select backfill and thus low in clay, organic matter, and salt content; these soils were typical of MSE wall backfill, but not likely representative of the broader variability of Florida waters and soils.

1.2.1 Literature review

In support of the overall project effort, literature surveyed under this effort included publications on MSE wall design and performance, mechanisms of concrete damage from direct exposure to air pollution and acidic rainfall, the structure and basis of quality assurance plans, and descriptions and comparisons of FDOT's methods (FMs) for corrosion properties with those of similar national methods. Also included in the literature review was an expanded discussion of pH measurement, with an emphasis on practical considerations for evaluating pH electrode performance in soil suspensions.

1.2.2 Trends in backfill properties

Trends in backfill properties were investigated to (1) identify sources and source regions of acceptable MSE wall backfill within FDOT's Districts 1 and 7, and for these districts (2) review databased results of MSE wall backfill (material 092L) for failure trends in pH, resistivity, chloride, and sulfate acceptance tests.

1.2.3 Single-laboratory contributions to method reproducibility

Single-laboratory contributions to method reproducibility of factors that relate to method field sampling and laboratory analysis were explored to improve method reproducibility through changes in sampling strategies, sampling processing, and analytical methods. Field sampling was used in the broadest sense to include sample collection, transport, and storage. Evidence-based recommendations for revisions to the FMs for pH, resistivity, chloride, and sulfate levels were proposed.

1.2.4 Replicate studies

Distributions of pH, resistivity, chloride, and sulfate levels within and between mines were estimated for select backfill based on replicate samples of mined soils. From these distributions were derived the method operating characteristic (OC) curves that form the basis of acceptance limits. Twelve replicate soil samples were collected at each of eight mines and these samples were characterized for geotechnical and corrosion properties by the USF soils laboratory.

1.2.5 Multi-laboratory contributions to method reproducibility

Multi-laboratory contributions to method reproducibility were estimated pre- and post-method revision to assess improvement in pH, minimum resistivity, chloride and sulfate measurements. Prior to method development, on-site testing of a select backfill was conducted at six FDOT and nine commercial laboratories, with representative laboratories in each FDOT district. Post-revision, six FDOT and the USF soils laboratory tested four materials that were candidates for select backfill as part of two consecutive inter-laboratory studies. From the inter-laboratory study results were prepared updated OC curves and a precision statement for each of the revised methods.

1.2.6 Geochemical modeling

Modeling under this task investigated the time it would take for infiltrating rainwater to alter significantly the corrosion properties of select backfill. Calculations were done with PHREEQC version 3, which is a publically-available model that was used to simulate one-dimensional transport of groundwater with multi-phase chemical equilibrium reactions.

1.2.7 Mine Information

Early in the project, two soils that met the requirements for select backfill—Starvation Hill and Santa Fe River— were collected from storage bins at FDOT's State Materials Office (SMO) in Gainesville. These soils served as proficiency test soils to gain experience with the FMs for pH, minimum resistivity, chloride and sulfate levels prior to collecting soil samples from mines. Over the project period, eight soils from as many mines were collected and transported back to the USF soils laboratory for geotechnical and corrosion property testing. The names and locations of mines that participated in this study were listed in Table 1-1.

Table 1-1 Mine Information

Mine ID	Date Sampled	FDOT District	Mine
1	05/08/2014	7	Transcor Dirt Services, LLC 16410 Balm-Wimauma Road, Wimauma, FL 33598
2	05/29/2014	1	Jahna Industries, Inc. 4910 SR 544, Haines City, FL 33844
3	06/19/2014	1	Youngquist Bros Rock Mine 15401 Alico Road, Ft. Myers, FL 33913
4	07/14/2014	1	C C Calhoun Mine, Pit # 7 3000 Bannon Island Road, Haines City, FL 33844
5	09/17/2014	7	Angelo's Recycled Materials 41111 Enterprise Road, Dade City, FL 33525
6	10/19/2014	1	Hickey Excavation, Inc. 7877 County Road 17S, Sebring, FL 33876
7	10/29/2014	5	Titan Florida Center Sand 16375 Hartwood Marsh Road, Clermont, FL 34711
8	11/12/2014	1	Cemex Alico Quarry 11840 Alico Road, Ft. Myers, FL 33913

1.3 Organization of Report

This report was organized along the lines of the contractual tasks, although not necessarily in the same temporal sequence. Tasks were mapped into chapters as follows:

- Literature review was divided into Chapter 2 Literature Review and Chapter 3 Measurement of Soil pH, Minimum Resistivity, Chloride and Sulfate;
- Trends in backfill properties were placed in Chapter 4 Trends in Select Backfill;
- Single-laboratory contributions to method reproducibility were split into four chapters, Chapter 5 Single Laboratory Precision and Bias, Chapter 7 Soil Sampling of Select Backfill, Chapter 8 Ruggedness Studies, and Chapter 9 Treatment and Other Studies;
- Replicate studies were placed in Chapter 11 Replicate Studies and Implications for Quality Assurance;
- Multi-laboratory contributions to method reproducibility were grouped into Chapter 6 Laboratory Visits and Chapter 10 Inter-Laboratory Study;
- Geochemical modeling was organized as Chapter 12 Geotechnical Modeling of Ion Transport in Sandy Soil; and
- Integration of project results occurred in Chapter 13 Revised Florida Methods for pH, Minimum Resistivity, Chloride, and Sulfate and Chapter 14 Summary and Recommendations

Proposed revisions were based on 2011 versions of FDOT FM 5-550 Florida Method of Test for pH of Soil and Water, FDOT FM 5-551 Florida Method of Test for Resistivity of Soil and Water, FDOT FM 5-552 Florida Method of Test for Chloride of Soil and Water, and FDOT FM 5-553 Florida Method of Test for Sulfate of Soil and Water. In this report further references to these methods are as FM for pH, FM for minimum resistivity, FM for chloride, and FM for sulfate, respectively.

2 Literature Review

2.1 Mechanically-Stabilized Earth (MSE) Walls

2.1.1 Features of an MSE wall and properties of select backfill

Mechanically-stabilized earth (MSE) walls have evolved over the past 40 years as a competitive replacement for reinforced concrete walls. MSE walls can be built to heights that exceed 25 m without the need of rigid foundation support and are advantageous where land availability is limited or at high cost, and where the ground is subject to slope instability or foundation soils are poor (Elias et al., 2001).

The features of an MSE wall are its pre-cast concrete facing panels built on a leveling pad and topped with a coping, and reinforcing elements attached to panels that extend behind the front face of the wall into select granular backfill or flowable fill, as shown in Figure 2-1 (Castellanos, 2012; FDOT, 2011). Construction of MSE walls with dry cast modular blocks is an option for lower retaining walls (Elias et al., 2001). Filter fabric installed behind the wall panels mitigates soil extrusion through the wall joints (Castellanos, 2012). Reinforcing elements are typically galvanized steel strips, but may also be grids, bar mats, welded or woven wire mesh of either galvanized steel or plain steel, or synthetic mesh of polypropylene, polyethylene, or polyester (Elias et al., 2001). Select granular backfill or flowable fill and reinforcing elements represent much of the construction cost (Elias et al., 2001).

Acceptable MSE wall backfill is characterized by high friction between the reinforcing element and backfill, good drainage, ease of emplacement and compaction, and low risk of microbiologically-induced corrosion (Elias et al., 2001). As such, backfill criteria generally exclude soils with significant clay or organic matter content. The Florida Department of Transportation (FDOT) requires that MSE wall backfill be a non-plastic soil, with a liquid limit less than 15, organic matter content not more than 2%, and gradation limits as shown in Table 2-1, with testing done per AASHTO T90, T89, T267, and T27, respectively (Scheer, 2013). Organic matter content is calculated as the average for three samples collected at each pit stratum or within each stockpile; if an individual sample exceeds 3% of the average, the pit stratum or stockpile is unsuitable (Scheer, 2013). In comparison, AASHTO (2012) limits the organic matter content to 1%.

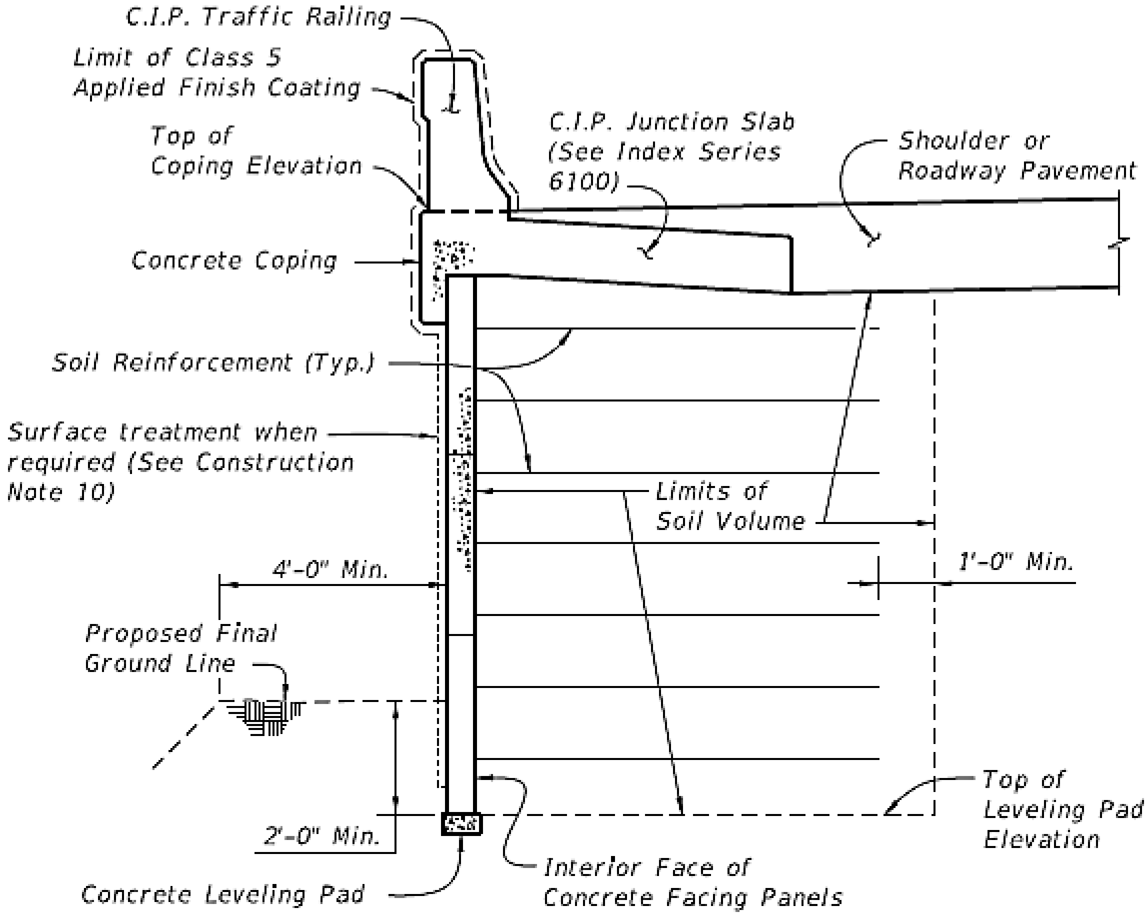


Figure 2-1. Schematic of a mechanically-stabilized earth (MSE) wall (FDOT, 2011).

Table 2-1 FDOT Gradation Limits for Backfill Used in Walls with Soil Reinforcements

Sieve Size	Percent Passing
88.9 mm (3-1/2 inches)	100
19 mm (3/4 inch)	70-100
No. 4	30-100
No. 40	15-100
No. 100	0-65
No. 200	0-12

The design life of an MSE wall is the period of time that the wall is expected to be in service as defined by service and strength conditions (AASHTO, 2012). The design life of MSE walls is typically 50, 75, or 100 yr (Fishman and Withiam, 2011); the FDOT mandates a minimum design life of 75 yr or 100 yr (FDOT, 2013). Choices for select granular backfill and reinforcing elements are critical in achieving the design life of MSE walls, and these choices are determined in large part by the potential for a pull-out failure of the reinforcing elements (AASHTO, 2012; Fishman and Withiam, 2011; Gladstone et al., 2006).

2.1.2 Corrosion of MSE wall reinforcement

Reinforcing elements made of metal, whether galvanized metal strips or plain steel mesh, once emplaced in soil are subject to corrosion. Variations in the soil environment can establish voltage potentials between adjacent metallic sites while soil pore water acts as an electrolyte for current flow between the sites (Jack and Wilmott, 2011). Key environmental factors that affect metal corrosion in soil include temperature, soil porosity, reduction/oxidation potential, water content, oxygen level, acidity or alkalinity, salt content, and microbial activity (Jack and Wilmott, 2011; Sagüés et al., 2009). To reduce the corrosion risk of metal reinforcing elements, elements are placed in backfill that is engineered to minimize corrosion. For example, backfill:

- Gradation limits provide for rapid drainage, low water retention, and soil aeration;
- Low organic matter content minimizes nutrient availability for microbial growth;
- Low water content reduces the opportunity for variations in oxygen levels within the soil that can lead to differential voltages and thus active corrosion sites;
- Low levels of salts and high soil resistivity keep low the corrosion currents; and
- Low levels of acids and bases minimize the potential attack of these chemicals on protective metallic oxide layers that in time coat the emplaced metal.

In Table 2-2 are shown the AASHTO and FDOT acceptance limits for soil pH, minimum resistivity, chloride and sulfate levels in compacted select backfill (Scheer, 2013).

Table 2-2 Acceptance Limits for Corrosion Properties of Compacted Select Backfill

Agency	pH	Minimum Resistivity, ohm-cm	Chloride, ppm	Sulfate, ppm
AASHTO	5 to10	3,000	<100	<200
FDOT	*5 to 9	3,000	<100	<200

*Exceptions allow for use of select backfill material with pH 4.5 to 5.0 per Scheer (2013).

Exceptions for use of select backfill material with pH 4.5 to 5.0 are as follows (Scheer, 2013):

- The interior face of MSE wall panels have 3 inches (760 mm) of concrete cover over the reinforcement; and
- For concrete used in the panels, the quantity of cement replaced with Type F fly ash is 10% to 20% by weight;
- The quantity of cement replaced with slag is 50% to 60% by weight;
- Portland cement is 30% by weight of total cementitious material;
- The total weight of Type F fly ash and slag does not exceed 70% of total cementitious material; and

- Metallic pipe must not be placed in backfill materials with pH < 5.

AASHTO's (2012) corrosion model for galvanized steel in MSE wall service is shown in Equation 2-1, where E_c is the thickness of metal at the end of service life, E_n is the nominal thickness of steel reinforcement at construction, and E_s is the sacrificial thickness of metal that is expected to be lost by uniform corrosion during the service life.

$$E_c = E_n - E_s \tag{2-1}$$

AASHTO applies to its model a 75-yr service life, an initial zinc thickness of 86 µm, a time of 2 yr for the initial zinc corrosion rate, and rates of 15 µm yr^{-1}, 4 µm yr^{-1}, and 12 µm yr^{-1} for the initial zinc, final zinc, and steel corrosion rates, respectively. This model yields 16 yr to loss of the zinc coating and a steel loss of 708 µm per side (AASHTO, 2012; Fishman and Withiam, 2011). FDOT's model is the same, except that FDOT's corrosion rates in mils yr^{-1} give a closer approximation than the AASHTO's corrosion rates in mils yr^{-1} to the above rates expressed in µm yr^{-1}; moreover, FDOT includes a steel corrosion rate of 7 µm yr^{-1} applied between 75 and 100 years for those walls with a 100-yr service life (FDOT, 2013).

In-situ and laboratory testing of in-service MSE wall reinforcing elements indicate that AASHTO's model is conservative, that is, it tends to over-predict corrosion losses of zinc in galvanized steel, when the select granular backfill material meets AASHTO's criteria for electrochemical parameters (Table 2-2) (Fishman and Withiam, 2011; Gladstone et al., 2006; Berke et al., 2008).

Fishman and Withiam (2011) investigated corrosion rates of reinforcing elements for 53 MSE walls in six states including Florida and applied a best-fit power law model (Equation 2-2) to describe the corrosion rate (*CR*) in µm yr^{-1} as a function of soil resistivity (ρ) in ohm-cm. Fishman and Withiam (2011) did not make clear for Equation 2-2 that the modeled data were for minimum resistivity, a distinction they made for Equation 2-1. MSE walls ranged in age from one to 30 yr with an average age of 13 yr; thus, corrosion rates largely reflected corrosion of the zinc coating. They found on the average, corrosion rates were 10 times higher for observations at sites with soil resistivity less than 3000 ohm-cm than for observations at sites with soil resistivity greater than 3000 ohm-cm.

$$CR \approx 1400\rho^{-0.75} \tag{2-2}$$

In simple terms, the presence of salt and water in soils provides a pathway for corrosion-inducing currents. All four of the soil electrochemical tests (Table 2-2) relate to soil salt content but Elias et al. (2009) found that the most reliable indicator of a soil's corrosion potential was minimum resistivity. Fishman and Withiam (2011) found that in reinforced fills, the condition of minimum resistivity < 3000 ohm-cm and pH < 5.0 significantly affected steel corrosion rates. Nevada's Department of Transportation (NDOT), for example, found that in two MSE walls, aged 9 yr and 25 yr, metal reinforcing elements were corroded such that the older wall required expensive mitigation (Thornley et al., 2010). NDOT attributed the cause to over-predicted soil resistivity based on Nevada's T235B conductivity method (NDOT, 1999) as compared to AASHTO's T288 minimum resistivity method.

Elias et al. (2009) reported that wide scatter in electrochemical test results were evidence of poor backfill conditions and recommended that sampling protocols include not only a minimum number of samples but also a maximum standard deviation in test results (Table 2-3). Moreover, their recommendation emphasized that samples for electrochemical testing be acquired with the help of an excavator to reach the interior top, mid, and bottom levels of a stockpile.

Table 2-3 Recommended Sampling Protocol for Electrochemical Testing of MSE Wall Backfill‡

Range of Minimum Resistivity ρ_{min}, ohm-cm	General Description	Preconstruction		During Construction	Comments
		Number of Samples	$\sigma_{resistivity}$, ohm-cm	Sample Interval, yd^3*	
>10,000	Crushed rock and gravel, < 10% passing No. 10 sieve	1 for resistivity; 3 for pH	NA	NA	(1) pH outside the specified limits is not allowed for any sample. (2) Backfill sources shall be rejected if ρ_{min} measured for any sample is less than 700 ohm-cm, chloride is > 500 ppm, or sulfate is greater than 1,000 ppm.(3) For materials with ρ_{min} < 5,000 ohm-cm, σ for chloride and sulfate shall be less than 100 ppm and 200 ppm, respectively.
5,000 to 10,000	Sandy gravel and sands	3 for resistivity; 6 for pH	<2,000	4,000 for resistivity; 2,000 for pH	
<5,000	Silty sands and clayey sand, screenings	5 for resistivity; 10 for pH	<1,000	1,000 for resistivity; 2,000 for pH	

‡Elias et al. (2009); *1 yd^3 = 0.7646 m^3

Reinforcing elements made of synthetic polymeric materials are also subject to degradation over time and the degradation rate, albeit slow for typical MSE wall construction, is influenced by material properties, reinforcement design, and environmental factors such as temperature, mechanical damage, stress levels, and chemical exposure (AASHTO, 2012). FDOT provides guidance on the suitability of synthetic reinforcing products for MSE walls (Scheer, 2013).

2.1.3 Susceptibility of concrete to damage from environmental exposures

Air pollution has been associated with damage to stone, mortar, cement, and concrete in both ancient and modern construction, especially in urban or industrial areas where acidic gases and catalytic particles may be present in relatively high concentrations (Lipfert and Daum, 1992; Hamilton and Crabbe, 2009; Roots, 2008; Sabbioni et al., 2001). Air pollutants commonly linked to materials degradation include sulfur dioxide, sulfuric acid, nitrogen oxides, nitric acid, ozone and its precursors, and aerosols (Hamilton and Crabbe, 2009). Concrete degradation is also caused by acid rain: rain, sleet, snow, ice, fog, and cloud water that have interacted with atmospheric carbon dioxide to form carbonic acid and with atmospheric pollutants such as sulfuric and nitric acids. Carbon dioxide although a natural constituent of the atmosphere, may be present at elevated concentrations in urban areas as a consequence of closely packed sources of fossil fuel combustion (Grimmond et al., 2002; Neville, 1996; Idso et al., 2002; Rice and Bostrom, 2011). Alkali dust, sea salt, and ammonia can neutralize acids present in the atmosphere and in rainfall (Hamilton and Crabbe, 2009).

In-service 20th-century concrete structures exposed to relatively high levels of air pollution have weathered crusts with evidence of carbonation, sulfur-attack, alkali-aggregate reactions, and cracking (Marinoni, et al., 2003; Ozga et al., 2011). Damage mechanisms to concrete include (1) dissolution and leaching of soluble components, (2) alterations that soften or weaken the concrete, and (3) formation of expansive constituents that can cause cracking. Studies that explore the interaction of dry- or wet-depositing pollutants on the properties of construction materials include one or more of these three research components: examination of in-service or retired structures, field or laboratory testing of specimens, and mathematical modeling of attack processes. Models tend to be calibrated against accelerated testing of concrete specimens in aggressive media on the assumption that this type of testing can adequately simulate long-term behavior (Marques and Costa, 2010; Rozière et al., 2009; Samson and Marchand, 2007). Summarized here were the general trends that appeared across these modes of study and that were relevant to the service life of MSE walls, with an emphasis on acid attack, carbonation, and sulfur attack.

Properties of concrete that are diminished over time by acid attack include loss of mass, loss of tensile and compressive strength, loss of flexibility, and elastic and dynamic modulus of elasticity, as examples (Fan et al., 2010; Zivica and Bajza, 2001). Acids that can severely damage concrete include inorganic acids: carbonic, hydrochloric, hydrofluoric, nitric, phosphoric, and sulfuric, and organic acids: acetic, citric, formic, humic, lactic, and tannic (Neville, 1996). Attack can be severe below pH 5.5, but the continued availability of the acid is as or more important than the pH in causing damage, because it takes time for the acid to penetrate the reacted product to the undamaged concrete (Beddoe and Dorner, 2005; Neville, 1996).

The general mechanism of acid attack in ordinary Portland concrete is summarized as follows (Beddoe and Dorner, 2005):

- Movement of protons (more precisely, hydronium ions H_3O^+) into the concrete;
- Dissolution of calcium hydroxide and calcium from calcium silicate hydrate (C-S-H) or calcium aluminum hydrate;
- Migration of the calcium towards the concrete surface; and
- Development of a concrete damage layer of predominantly hydrated silicates.

The solids that dissolve and precipitate as the acid attack proceeds depend upon the counter anion (carbonate, sulfate, and nitrate as examples), the salts and minerals present in the concrete, and the concrete pore solution pH (Beddoe and Dorner, 2005). Under some conditions, precipitating solids such as calcium carbonate and calcium sulfate can reduce the pore volume and slow acid diffusion; some solids, including calcium chloride and calcium nitrate, have relatively high water solubility and readily leach in pore water (Beddoe and Dorner, 2005; Zivica and Bajza, 2001).

Acidic gases—carbon dioxide, sulfur dioxide, and nitric acid, as examples—can diffuse faster and further into concrete than their aqueous counterparts, but ultimately require water for the attack to proceed (Okochi et al., 2000). Concrete pore water can help or hinder acid attack: too much pore water and diffusion rates slow; too little water and reaction rates slow; attack rates are optimized when the relative humidity is between 50% and 75% (Zivica and Bajza, 2001). Wet and dry cycling may damage concrete faster than conditions that are consistently either wet or dry (Beddoe and Dorner, 2005; Gruyaert et al., 2012; Sersale et al., 1998; Xie et al., 2004); Okochi et al. (2000), however, found that neutralization depth was greater in sheltered than in unsheltered concrete after a 2-yr exposure to ambient air pollution. Neutralization depth (Okochi et al., 2000) and strength loss (Cao et al., 1997; Xie et al., 2004) was proportional to proton concentration in test specimens.

Properties of concrete such as the ratio of water to cement (W/C), alkali and sulfur content, aggregate material, and additives may enhance or retard acid attack. For example, higher W/C ratios tend to increase attack rates due to the increased availability of water (Sersale et al., 1998), but larger pore volumes may mitigate the damage due to expansive mineral formation (Jacques et al., 2010). The presence of sodium or potassium hydroxides may increase attack rates as the dissolved alkali diffuse readily to the concrete surface. The use of acid-resistant aggregate and aggregate with a greater content of small particles that can reduce concrete pore volume tend to reduce attack rates (Zivica and Bajza, 2002). Pozzolans such as fly ash or silica fume can convert calcium hydroxide to C-S-H, which can increase the concrete density and slow acid diffusion and thus reduce a concrete's vulnerability to acid attack, or pozzolans can by lowering the calcium hydroxide content reduce the amount of acid needed to lower the pore water pH and thus increase the damage (Neville, 1996). Replacement of cement with blast furnace slag in Portland concrete resulted in a concrete with lower calcium oxide but higher silica dioxide content that was more resistant to acid attack (Gruyaert et al., 2012).

Carbonation of ordinary Portland concrete occurs when water-dissolved carbonic acid reacts with calcium hydroxide in concrete to form calcium carbonate and water (Rozière et al., 2009; Steffens et al., 2002: Zivica and Bajza, 2001). Calcium hydroxide is present in concrete paste at concentrations of 20% to 25% by volume (Mindess et al., 2003). Once calcium hydroxide has been carbonated, the pH of the concrete pore water drops from ~13 to ~9. At pH 9, the passivation layer on reinforcement steel is removed. If oxygen and moisture are present, removal of the passivation layer allows corrosion of the steel and formation of expansive corrosion products that can lead to cracking (Mindess et al., 2003; Neville, 1996). Carbonation progresses at a rate proportional to $yr^{0.5}$, but the rate depends on internal factors such as concrete porosity and moisture content, and external factors such as atmospheric carbon dioxide concentration and temperature (Duffó et al., 2012; Neville, 1996). Over a 75-yr lifetime in good quality concrete the carbonation depth is on the order of 2 to 9 mm (Duffó et al., 2012); a carbonation of depth of 15 mm in 16 yr has been observed in low quality concrete (Neville, 1996). Observed carbonation rates may increase over the next century if global trends in atmospheric carbon dioxide concentrations and temperatures continue (Yoon et al., 2007). Carbonation tends to increase both the tensile and compressive strength of concrete but it also increases shrinkage, which can lead to crack formation (Mindess et al., 2003); precipitates from the carbonation process may also clog concrete pores and form a protective zone (Glasser et al., 2008).

Concrete structures are exposed to sulfate from atmospheric sulfur dioxide, from sulfuric acid on aerosols or dissolved in rainwater, or from sulfuric acid or sodium sulfate in groundwater, as examples. The American Concrete Institute (ACI, 2011) has divided sulfate exposure into categories and classes (Table 2-4). When exposed to sulfate, concrete can undergo a reaction that precipitates gypsum, ettringite, and thaumasite, or mixtures of these solids (Cao et al., 1997; Glasser et al., 2008; Neville, 1996). Thaumasite formation requires not only sulfate and C-S-H, but carbonate in solution (Glasser et al., 2008). The presence of gypsum and thaumasite is associated with loss of material strength and adhesion, and the presence of ettringite with localized pressure that leads to concrete cracking (Cao et al., 1997; Collepardi, 2003). Collepardi (2003) emphasizes that three conditions must be met for ettringite formation: high permeability concrete, a sulfate-rich environment, and the presence of water. The concentration and species of dissolved ions such as protons, sodium, potassium, calcium, and magnesium influence mineral formation and leaching (Fan et al., 2010; Glasser et al., 2008; Kanazu et al., 2001). (Sulfur may also be present in the starting materials of concrete and under some conditions during the lifetime of the concrete may dissolve and re-precipitate as ettringite.)

Table 2-4 Sulfate Exposure Categories and Classes (ACI, 2011)

Severity	Class	Condition	
		Water-soluble sulfate in soil, % by mass	Dissolved sulfate in water, ppm
Not applicable	S0	sulfate < 0.10	sulfate < 150
Moderate	S1	0.10 ≤ sulfate < 0.20	150 ≤ sulfate <1500
Severe	S2	0.20 ≤ sulfate ≤ 2.00	1500 ≤ sulfate ≤10,000
Very severe	S3	sulfate > 2.00	sulfate > 10,000

Stark (2002) found that low ratios of W/C provided the greatest resistant by concrete to sulfate attack. Concretes that are prepared with pozzolanic cements such as metakaolin, silica fume, blast furnace slag, and fly ash have lower permeability and offer resistance to sulfate attack (Cao et al., 1997; Djuric et al., 1996), except that fly ash amendment may not protect against thaumasite formation (Glasser et al., 2008). Results conflict for blast furnace slag and silica fume, which is a possible consequence of varied approaches and scenarios for accelerated testing (Cao et al., 1997; Gruyaert et al., 2012; Stark, 2002). Cement replaced with blast furnace slag in Portland concrete was more susceptible to carbonation during an accelerated test for sulfate attack, and damage from sulfate attack was more severe with high replacement levels of blast furnace slag (Gruyaert et al., 2012).

One approach to assessing the impact of environmental exposure on concrete durability is from a dose-response relationship, where dose refers to the exposure of the concrete to an air pollutant(s) and is proportional to air pollutant concentration x exposure time, and response is a corresponding loss of concrete mass or function. Dose and response relationships can be established from experiments in a controlled setting (Fan et al., 2010; Jacques et al., 2010) or measured under natural conditions (Tidblad, et al., 1998; Roots, 2008). Whether simulated or natural, the temporal pattern of weather phenomena such as temperature, rainfall rate and amount, and relatively humidity plays an important role in concrete degradation.

Table 2-5 shows ion concentrations in weekly rainfall that was collected at a National Atmospheric Deposition Program (NADP) National Trends Network (NTN) FL 41 site in Sarasota County, Florida (27.38 N, 82.28 W). For the period 2000 to 2012, the median, minimum, and maximum pH values at this site were 5.01, 3.99, and 6.59, respectively; pH 7 is neutral, so this rainfall was acidic (NADP, 2013). The median pH of rainfall observed at this site was typical for NADP NTN sites across Florida (NADP, 2013).

Table 2-5 Ion Concentrations (ppm) in Weekly Rainfall Collected between 2000 and 2012 at NADP's NTN FL 41 Site in Sarasota County, Florida

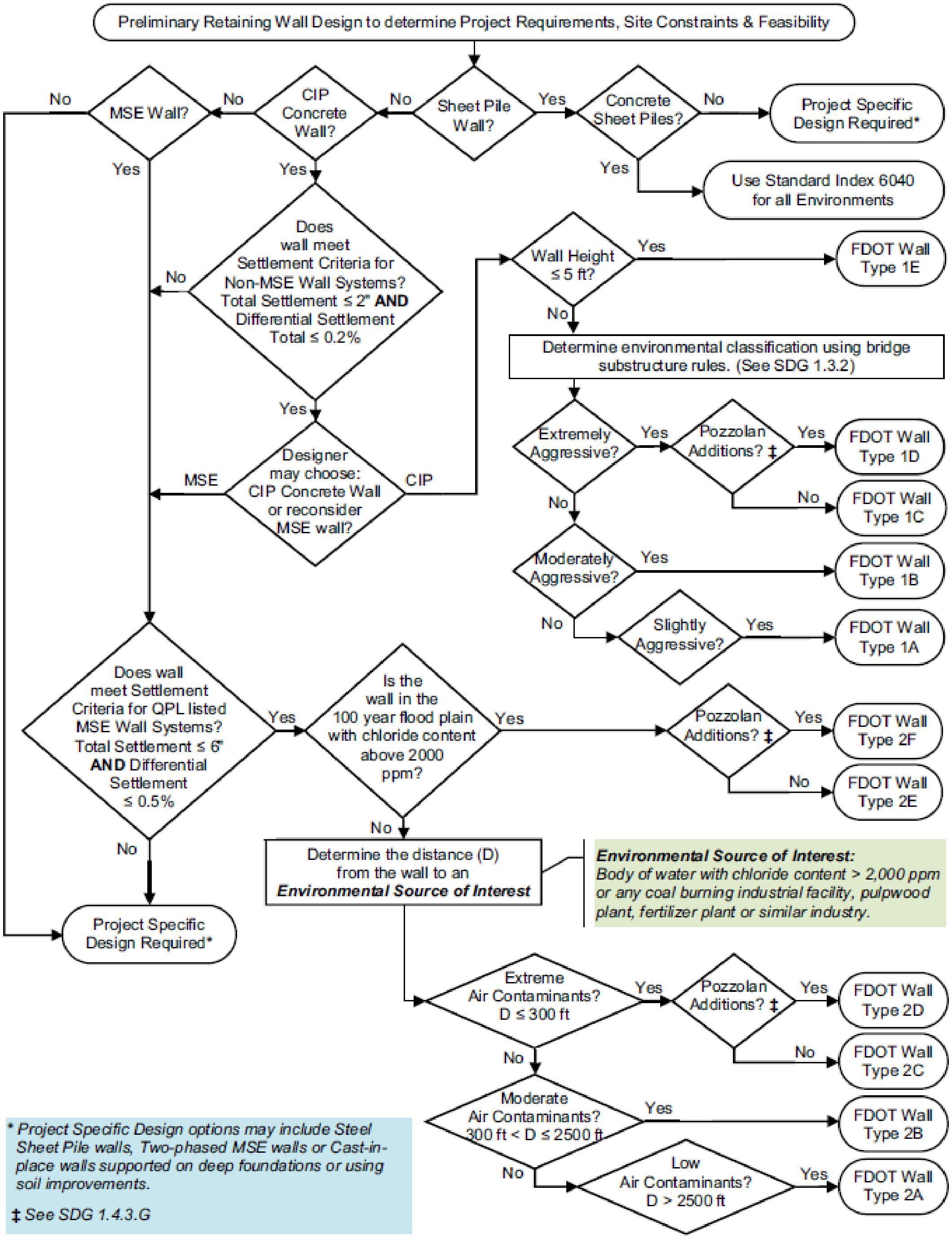
Statistic	pH Lab	Ca^{2+}	Cl^-	K^+	Mg^{2+}	Na^+	NH_4^+	NO_3^-	SO_4^{2-}
Median	5.01	0.125	0.626	0.026	0.049	0.345	0.123	0.684	0.820
Minimum	3.99	0.010	0.027	0.003	0.003	0.010	0.006	0.020	0.120
Maximum	6.59	1.29	8.8	0.300	0.639	5.83	1.23	5.60	5.27

NADP's NTN sites were intentionally located outside the direct influence of one or more air pollution sources such as a power plant plume, but in urban areas concentrations of pollutants in rainfall may be higher. For example, Strayer et al. (2007) observed lower pH and higher chloride and sulfate concentrations in rainfall measured at the eastern end of the Gandy Bridge in Tampa, Florida (27.85 N, 82.55 W) between 1996 and 2004. For comparison, at the Gandy Bridge site the median, minimum and maximum values were, respectively, 4.5, 3.4, and 6.0 for pH; respectively; 1.48, 0.19, and 14.3 ppm for chloride concentrations, respectively; and 2.09, 0.19, 15.8 ppm for sulfate concentrations, respectively. Even for urban Tampa, however, sulfate concentrations did not pose a threat to concrete of sulfate attack (Table 2-4).

Tidblad et al. (1998) developed a dose-response curve for unsheltered Portland limestone exposed to air pollution (Equation 2-3), where R is the surface recession (depth to undamaged surface) in µm, t is time in yr (1 to 8 yr), SO_2 is the sulfur dioxide ambient air concentration in µg m^{-3} (1 to 83 µg m^{-3}), T is temperature in ^{o}C (2-19 ^{o}C), *Rain* is rainfall in mm (327-2144 mm), and H^+ is the proton concentration in ppm (0.0006 to 0.13 ppm).

$$R = t^{0.96}(2.7[SO_2]^{0.48}\exp\{-0.018T\}+0.019Rain[H^+]) \qquad (2\text{-}3)$$

Average values for urban Tampa were substituted into Equation 2-3: t = 8 yr, SO_2 = 50 µg m^{-3} (USEPA, 2013), T = 19 ^{o}C, *Rain* = 1200 mm, and H^+ = 0.032 ppm (Strayer et al., 2007) for a surface recession R of 98 µm or ≅ 0.1 mm. An updated formulation of the dose-response curve for Portland limestone published by Roots (2008) included the combined effects of relative humidity, sulfur dioxide, nitric acid, aerosols, and rainfall acidity and yielded a surface recession R of ≅ 0.3 mm for Tampa conditions. From the dose-response relationship, average urban Tampa air pollution does not appear to pose a threat to MSE wall concrete, with the caveat that air pollutant concentrations in the vicinity of power plants or industrial facilities such as sulfuric acid or nitric acid manufacturing plants may pose a significant risk. To address this risk, FDOT (2013) specifies amendment of structural concrete with pozzolans (silica fume, metakaolin, or ultrafine fly ash) (Figure 2-2, Table 2-6).



Environmental Source of Interest:
Body of water with chloride content > 2,000 ppm or any coal burning industrial facility, pulpwood plant, fertilizer plant or similar industry.

** Project Specific Design options may include Steel Sheet Pile walls, Two-phased MSE walls or Cast-in-place walls supported on deep foundations or using soil improvements.*

‡ See SDG 1.4.3.G

Figure 2-2. Permanent retaining wall selection process flowchart.

Table 2-6 FDOT MSE Retaining Wall Classification

Durability Requirements					Other Allowable FDOT Wall Types					
Applicable FDOT Wall Type	Concrete Cove (in)*	Concrete Class for Panels	Pozzolan Additions? **	Soil Reinforcement Type	2A	2B	2C	2D	2E	2F
Type 2A	2	II	No	Metal		✓	✓	✓	✓	✓
Type 2B	2	IV	No	Metal			✓	✓	✓	✓
Type 2C	3	IV	No	Metal				✓	✓	✓
Type 2D	3	IV	Yes	Metal					✓	✓
Type 2E	3	IV	No	Plastic						✓
Type 2F	3	IV	Yes	Plastic						

*1 in = 25.4 mm; **Silica fume, metakaolin, or ultrafine fly ash

2.2 Quality Assurance (QA) Plans for Construction Materials

Quality assurance (QA) plans devised for construction materials support an overall project goal to build a structure of known integrity and service life. Burati et al. (2003) outlined five basic steps to creating or modifying a QA plan:

- Assimilate data and information to determine relevant construction parameters;
- Establish the desired level of quality for construction materials;
- Design a QA plan, including acceptance quality characteristics (AQC), statistical quality measures, buyer's and seller's risks, lot size, number of samples, acceptance limits, and payment-adjustment provision;
- Monitor how the plan performs; and
- Make adjusts as necessary.

The ultimate goal of a change to a QA plan is to improve product quality, speed project completion, reduce risk, or lower bid cost (Burati et al., 2003).

Quality assurance (QA) plans for MSE wall materials are intended to reduce the risk of an early wall failure. Select backfill is a critical component of an MSE wall and thus properties of select backfill such as particle size gradation, organic matter content, plasticity, liquid limit, and corrosion have been identified as important acceptance quality characteristics (AQC) (Scheer, 2013). Our research had as its focus the AQC for corrosion—pH, minimum resistivity, chloride and sulfate levels—and was motivated by a material rejection frequency that was too high for one or more of these AQC. Under consideration were the AQC, statistical measures, risk, lot size or soil type, number of samples, and acceptance limits but not payment-adjustment provisions, which were beyond the research scope.

2.2.1 Acceptance quality characteristics (AQC) for corrosion tests

Acceptance quality characteristics (AQC) are embedded in a QA plan that includes both process (quality) control and product acceptance (Burati et al., 2003). Figure 2-3 illustrates FDOT's process control for pH of select backfill, as an example. Test results for material process control and product acceptance depend not only on the written procedures of a test method but also on a broader suite of influences such as material properties, physical infrastructure, laboratory practices, operator training, costs versus payments, and so forth (Burati et al., 2003). These influences manifest themselves as bias and (im)precision in test results. Process control and product acceptance limits for select backfill corrosion AQC such pH, minimum resistivity, chloride, and sulfate levels include a margin of safety, which was initially established based on statistical inference drawn from test data that capture the relative (im)precision due to these influences. Equation 2-4 offers a perspective on how variability (or error) in test results is partitioned (Burati et al., 2003; Mason, 1992). Sampling error, however, is often the largest contributor to total error (Mason, 1992). Standards such as AASHTO T2 and T248 intend to reduce systematic error associated with sampling and process, respectively; certification of Qualified Sampling Technicians (QSTs) also aims to reduce systematic error associated with sampling. Test methods such as the FM for pH help to minimize systematic errors due to testing; use of qualified or certified operators and/or laboratories, reference materials or split samples, and control charts are additional strategies for mitigating systematic error due to testing (Burati et al., 2003).

$$\sigma_{total}^2 = \sigma_{material}^2 + \sigma_{environment}^2 + \sigma_{sampling}^2 + \sigma_{process}^2 + \sigma_{testing}^2 \qquad (2\text{-}4)$$

Verification is a key aspect of process control and product acceptance. Burati et al. (2003) distinguishes between verification of test method and product, where the former is done through a comparison of a split samples—that is, subsamples of the same material—and the latter is done through a comparison of independent samples. For verification, one simple approach is to apply the 'D2S limits' or the maximum acceptable difference between test results, where the D2S limits represent the 95% confidence interval for individual results and may be derived from test method inter-laboratory studies (ASTM C670). If the difference between agency or engineer and contractor test results is within the D2S limits, for example, the contractor's test is verified. Where replicate tests of independent samples are available, a difference between agency or engineer and contractor results can be inferred from a *t*-test on the averages and an *F*-test on the variances.

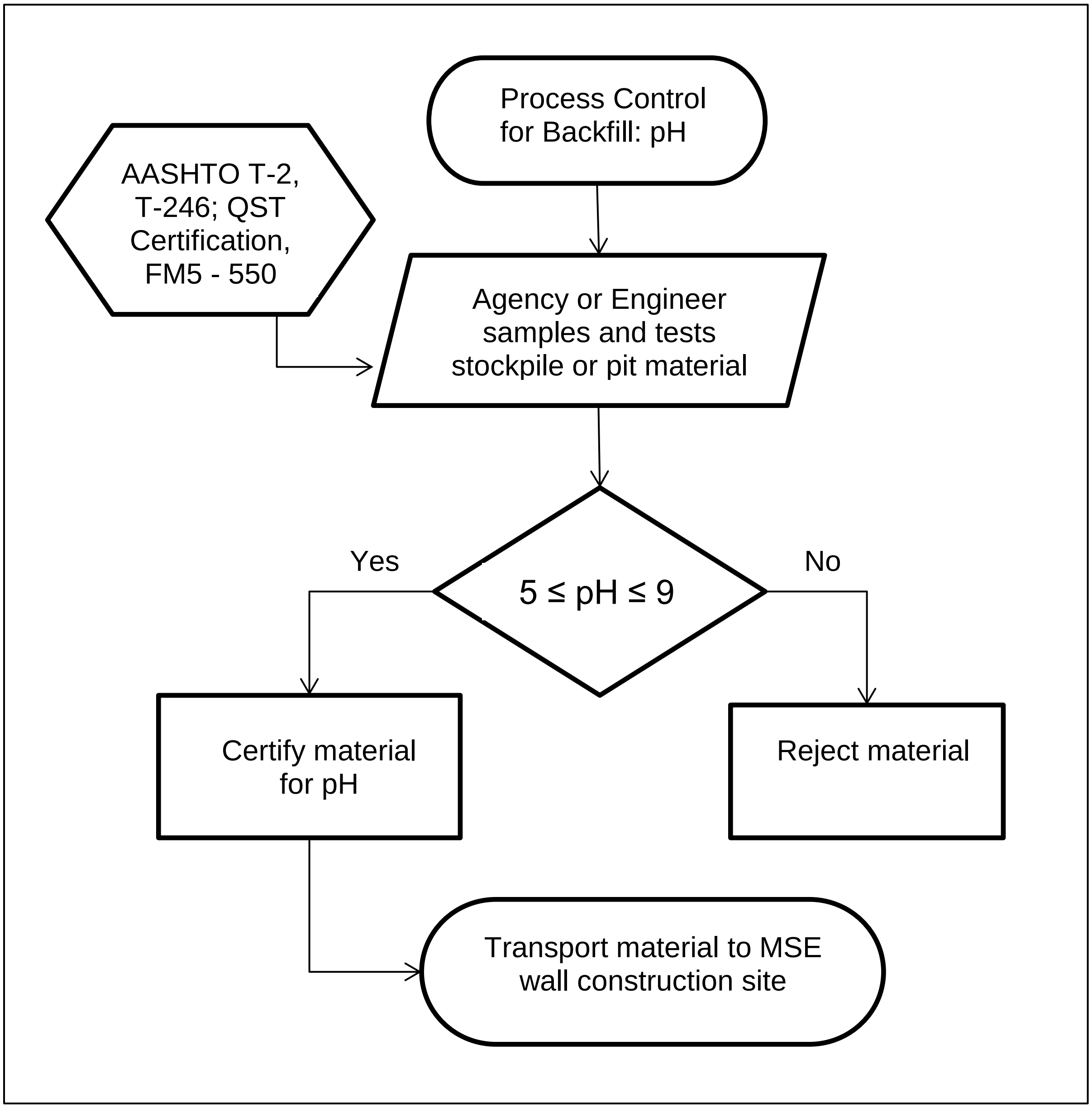


Figure 2-3. Process control for pH of select backfill for MSE walls with metallic reinforcement.

The basis of a process control or acceptance test limit is an operating characteristic (OC) curve, which in some way relates test error, ideally $\sqrt{\sigma_{total}^{2}}$ (Equation 2-4), to risk. Burati et al. (2003) referred to a Type I (α) error as the seller's risk—the risk the contractor has that a product is rejected—and a Type II (β) error as the buyer's risk—the risk the agency has in accepting a faulty product. Burati et al. (2003) provided a summary table of suggested risk levels based on AASHTO R9 (Table 2-7).

Table 2-7 Suggested Risk Levels (AASHTO R-9)

Degree of Importance	Recommended Type I (α) error	Recommended Type II (β) error
Critical: Essential to the preservation of life	0.050	0.005
Major: Necessary for the prevention of substantial financial loss	0.010	0.050
Minor: Does not materially affect performance	0.005	0.100
Contractual: Provides uniform standards for bidding	0.001	0.200

Although not explicitly stated in FDOT guidance documents, the process control and product acceptance limits for minimum resistivity, chloride, and sulfate (Table 2-2) likely have a margin of safety. The criteria for substructure environmental classification as it applies to steel exposed to minimum resistivity in soil are as follows: <1,000 ohm-cm, extremely aggressive; >5,000 ohm-cm, slightly aggressive; and between 1,000 and 5,000 ohm-cm, moderately aggressive (FDOT, 2013). A 3,000 ohm-cm minimum resistivity for MSE wall backfill falls within the range of moderately aggressive (Scheer, 2013). The criteria for substructure environmental classification as it applies to steel exposed to chloride concentrations in soil are as follows: >2,000 ppm, extremely aggressive; <500 ppm, slightly aggressive; and between 500 ppm and 2,000 ppm, moderately aggressive (FDOT, 2013). A 100-ppm chloride concentration falls within the range of slightly aggressive (Scheer, 2013). Finally, the criteria for substructure environmental classification as it applies concrete exposed to sulfate concentrations in soil are as follows: >2,000 ppm, extremely aggressive; <1000 ppm, slightly aggressive; and between 1,000 ppm and 2,000 ppm, moderately aggressive (FDOT, 2013). A 200 ppm sulfate concentration falls within the range of slightly aggressive (Scheer, 2013). Thus, in the development of OC curves for minimum resistivity, chloride, and sulfate levels, the assumed critical (rejection) limits were 1,000 ohm-cm, 500 ppm, and 1,000 ppm, respectively.

Environmental classification for soil pH between steel substructures and MSE wall backfill are incongruous. The criteria for substructure environmental classification as it applies to steel exposed to pH in soil are as follows: <6 pH units, extremely aggressive; >7 pH units, slightly aggressive; and between 6 and 7 pH units, moderately aggressive (FDOT, 2013). For MSE wall backfill, pH must fall between pH 5 and pH 9 for metal reinforcement and between pH 4.5 and pH 9 for geosynthetic reinforcement (Scheer, 2013). According to Elias et al. (2009), "corrosion literature suggests that for bare steel and pH between 4 and 10, the corrosion rate is independent of pH and depends only on how rapidly oxygen diffuses on the metal surface." Soils that have a pH 4 or less are considered extremely acidic and soils that have a pH 10 or greater are considered extremely alkaline. Thus, in the development of an OC curve for pH, the assumed lower and upper critical (rejection) limits (for metal reinforcement) were pH 4 and pH 10, respectively.

A method operating characteristic (OC) curve can be constructed to show the probability of accepting a good material (1-β) versus rejection and acceptance limits, as was shown for pH in Figure 2-4. Development of this OC curve assumed sampling and analysis for pH of two independent and random samples (N = 2), a Type I (α) error of 0.010 and a Type II (β) error of 0.05 (Table 2-7), rejection limits of pH 4 and pH 10, and acceptance limits of pH 5 and pH 9 (Table 2-2). Also shown in Figure 2-4 was the impact of test error σ on the OC curve. Refer to Chapter 11, Section 11.2.4, for an explanation of the calculations behind the OC curve. For the conditions modeled, the OC curve in Figure 2-4 indicated that for σ > 0.4, the buyer's statistical power for accepting a good backfill was lower than the target probability of 0.95 or 95% (solid horizontal line). In this example, several options were available to improve the buyer's risk: (1) change the acceptance limits, (2) increase the number of samples, (3) reduce the test error, (4) shift more risk to the seller, (5) or modify the reinforcement design or material.

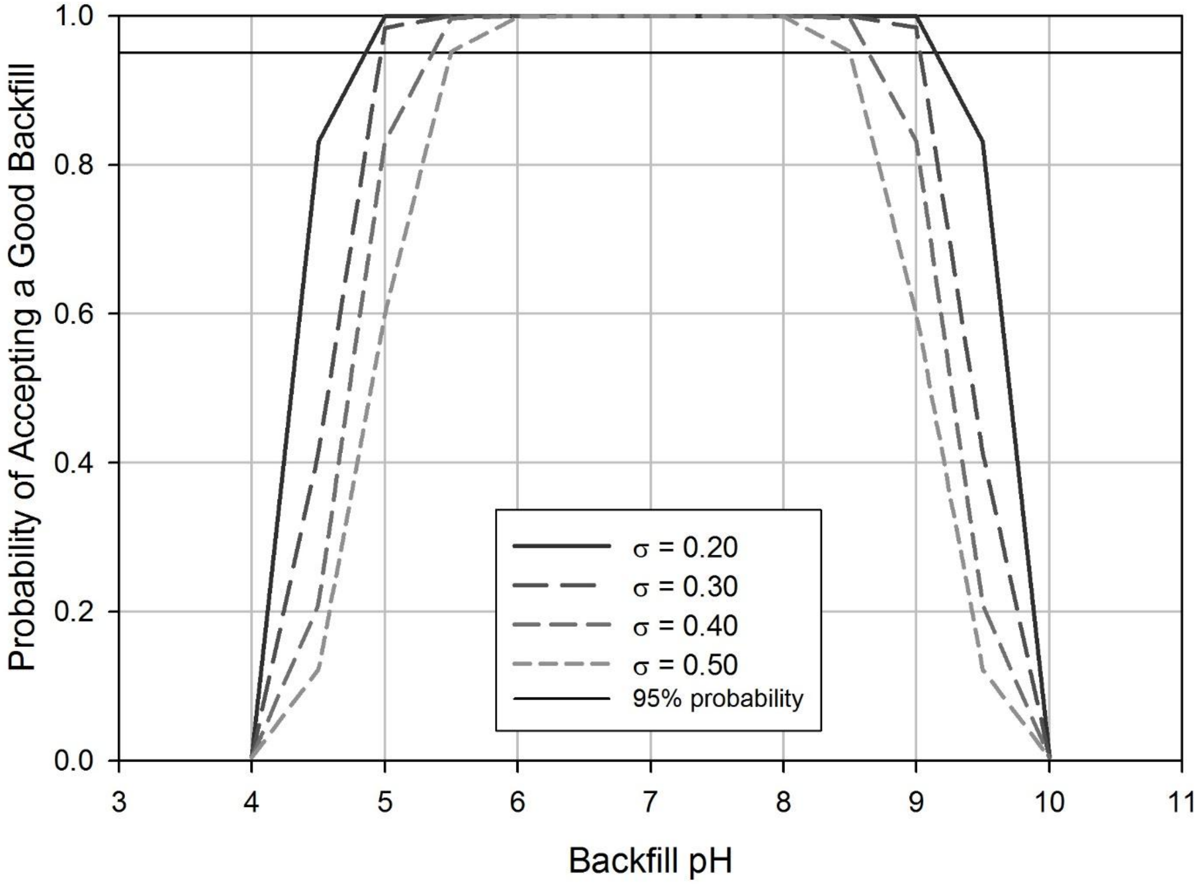


Figure 2-4. Example operating characteristic (OC) for pH N = 2.

2.2.2 FDOT’s QA plan for select backfill corrosion AQC

FMs for pH, minimum resistivity, chloride, and sulfate began as field tests for environmental characterization at bridge sites but over time evolved to laboratory-based tests, especially as specifications co-evolved to use the results for AQC acceptance tests. Laboratories that run the FMs for pH, resistivity, chloride, and sulfate are at present neither certified by FDOT nor accredited through AASHTO, although a laboratory may be accredited by AASHTO to run similar AASHTO tests. CMEC, which is a company that specializes in construction accreditation, education, and certification, may upon request inspect a laboratory for soil corrosion tests, but this inspection is not recognized by FDOT. Commercial laboratories that do soil corrosion testing are typically well-known in the construction industry and have offices convenient to district construction activities. FDOT may assist with preliminary sampling of a potential MSE wall backfill source but neither certifies the backfill nor accepts the emplaced material.

2.2.2.1 Process control for corrosion AQC

Sources of MSE wall backfill include borrow pits or stockpiles from construction sites, excavations by individual land owners or non-mining businesses, commercial yards that sell construction materials, and commercial mines. A stockpile, portion of a stockpile, or stratum in a borrow pit is identified as candidate material for MSE wall backfill in response to a project need. Upon request by the Construction Engineering and Inspection (CEI) personnel, a qualified sampling technician (QST) collects a sample of the material at the stockpile or pit per AASHTO T2 and T248. This sample is returned to a laboratory and processed and tested in accordance with AASHTO T248 and the FMs for pH, minimum resistivity, chloride, and sulfate. The QST may be an independent contractor or may be an FDOT employee. If testing indicates that the material meets the requirements for MSE wall backfill, the test results are certified, that is, signed and sealed by a Florida Professional Engineer, and the source certification is provided to the CEI. Ideally, these test results are entered into FDOT’s Laboratory Information Management System (LIMS). For corrosion AQC, certification is based on analysis of one sample and on test results that are within the acceptance limits shown in Table 2-2. In FDOT’s Districts 1 and 7, certified test results are transferable between projects if the test results are less than five years old; in other districts, separate testing and certification may be required for each project. The laboratory that does the testing for stockpile or borrow pit certification must be different from the laboratory that does the product acceptance testing. Refer to Figure 2-3 for a simplified schematic of process control for pH.

2.2.2.2 Product Acceptance for Corrosion AQC

When the certified MSE backfill is trucked from its source to the construction site, a separate on-site stockpile is created for the material. Upon arrival of the backfill at the site a delivery ticket is given to the contractor, and the ticket includes information about the source. An on-site CEI may keep a sample of the backfill material by source in a clear plastic bag to compare with the delivered material or to help identify soil type for testing purposes. Key construction personnel maintain the knowledge of on-site stockpiles by source. On-site stockpiles of MSE wall backfill are consumed typically within days to weeks. Backfill is emplaced and compacted in lifts in the MSE wall, and water may be added during the compaction process. Water quality must meet the same requirements as water for concrete (Scheer, 2013). Acceptance samples are taken after backfill has been emplaced (Scheer, 2013). A sample of backfill is shoveled into a bucket or bag from a compacted lift, usually a lower lift and early in the emplacement process. One bag contains backfill for many tests, among which are the corrosion tests. In Districts 1 and 7, however, a subsample is placed in a plastic bag and transferred in a cooler to the laboratory for pH testing, a practice that is consistent with the FM for pH. Samples for corrosion and other testing are accompanied by a completed C-22 form that describes the sampling details.

The contractor is compelled to obtain one backfill sample per soil type; this is a quality control sample, which is coded in LIMS as sample type ‘Q’. The CEI is compelled to obtain an independent verification sample, which is coded ‘V’ in LIMS. Both ‘Q’ and ‘V’ samples are part of product acceptance. The ‘V’ sample is obtained at the same sampling frequency, but ideally at a different time and location than the ‘Q’ sample. The ‘Q’ and ‘V’ samples are tested by different laboratories. If there is a failure of either the ‘Q’ or the ‘V’ sample, a split sample of the ‘Q’ sample is re-tested by a third laboratory as a resolution sample, which is coded ‘R’ in LIMS. The CEI may request a FDOT laboratory to test a ‘V’ or an ‘R’ sample. Laboratories enter the corrosion test results and data provided on the C-22 form directly into LIMS.

2.2.3 Sampling of select backfill

Sampling is a source of systematic error in corrosion test results (Equation 2-1). Intrinsic to the material sampled and the equipment used for sampling is “sample correctness,” which Mason (1992) describes as “when all particles in a randomly chosen sampling unit have the same probability of being selected for inclusion in the sample.” Failure to observe sample correctness introduces systematic error or bias in test results. This bias may be small for homogeneous soils or strata but large for heterogeneous soils. Other sampling errors relate to the heterogeneity of the material, fluctuations and segregation of material properties, and extraction error (Mason, 1992). Error associated with the inherent heterogeneity of a soil, for example, can only be diminished by grinding the material to a finer particle size or testing a larger sample. Errors associated with fluctuations and segregation of material property, for example, particle size segregation or chemical gradients, can be reduced by combining and mixing random subsamples to form a representative composite sample. Extraction error relates the geometry of the sampling unit to the sampling device; to properly sample a 2-dimensional soil stratum, for example, a cylindrical core should penetrate the entire depth of the stratum (Mason, 1992).

FDOT has developed a training and certification program to minimize sampling errors. A person sampling soil for MSE wall backfill must be an FDOT Qualified Sampling Technician (QST), trained in the performance of AASHTO T2 (ASTM D75), modified by FDOT FM1-T002, and T 248 (ASTM C702). QST training includes much more detail with regard to strategies for sampling of stockpiles than is given in AASHTO T2. AASHTO T2 is a standard practice for sampling aggregate and AASHTO T248 is a standard method of test for reducing samples of aggregate to testing size. AASHTO T2 is broadly applicable for aggregate from 2.36 mm to 90 mm in diameter; its implicit focus is sampling to characterize the aggregate size gradation. Procedures in AASHTO T2 in common with the FMs for pH, minimum resistivity, chloride, and sulfate are

- Obtain a representative sample;
- Avoid the outer surface or disturbed surface (overburden for a pit or bank); and
- Transport the sample to preclude loss or contamination of sample or damage to contents from mishandling.

For sampling stockpiles, pits or banks, and truck loads of coarse or coarse plus fine aggregate, the AASHTO T2 practice include in general

- Design a sampling plan for specific case under consideration;
- Define the number of samples to represent lots and sub lots of specific sizes;
- Determine the number of field samples to give the desired confidence in test results;
- Collect a minimum sample mass is 10 kg for aggregate 2.36, 4.75, and 9.5 mm in diameter;
- Label individual shipping containers with sample ID to facilitate sample field and laboratory reporting; and
- Document the supply location, approximate quantity of supply, quantity and quality of overburden, length of haul to worksite, character of the haul, and details of the extent and location of material represented by each sample.

For stockpiles:

- Use power equipment to separate into a small sampling pile materials drawn from various locations and levels of the main pile after which several increments may be combined to compose the sample – or – draw several samples from separate areas of the pile; if no power equipment are available take three increments from the top third, the middle third, and the bottom third of the pile;
- Use sampling tubes 30-mm diameter x 2-m long; and
- Take a minimum of 5 increments from random locations.

For pits or banks:

- Identify different stratum and select samples from each stratum;
- Drill or excavate holes to look for variation in quality ;

- Channel the face vertically to obtain samples; and
- Mix and quarter samples to obtain at least 12 kg (of sand).

Field sampling instructions in common to FMs for pH, minimum resistivity, chloride, and sulfate address not only sampling error but also systematic error introduced from sample processing and from environmental conditions (Equation 2-1):

- Obtain a representative sample;
- Use clean tools;
- Avoid or reduce excessive moisture;
- Avoid the weathered or vegetated surface;
- Place a minimum of 1 kg in a plastic or plastic-lined bag;
- Minimize the contact of collected soil with air;
- Store and transport the soil in cool, dark conditions; and
- Store up to 7 days at 4°C; do not freeze (pH, chloride, and sulfate methods).

2.2.4 Good laboratory practices

Once a sample reaches the laboratory, general laboratory practices are among those influences that contribute either directly or indirectly to systematic error of test results. Good laboratory practices (ASTM D3856) include

- A workspace that is clean, comfortable, and safe;
- Staff that have education and training appropriate for assigned tasks;
- Written procedures that provide clear direction for sample collection, handling and storage, sample analysis, and calibration and maintenance of the measurement system;
- Supervision of laboratory staff to promote uniform and compliant performance of procedures;
- Recordkeeping to document equipment calibration, repair, and maintenance;
- A chemical hygiene plan;
- A system for tracking sample disposition and analyses;
- Recordkeeping to document QA/QC activities; and
- Communication and troubleshooting protocols for investigating out-of-control results.

Additional quality assurance and quality control (QA/QC) measures are often part of materials testing. These measures may be implicit—part of good laboratory practices such as checking the calibration of an analytical balance or the conductivity of the water generated by a deionization system—or explicit in a test method. Typical laboratory QA/QC activities are shown in Table 2-7 (ASTM D3856; FDEP, 2009).

Table 2-8 Typical Laboratory QA/QC Activities

Activity	Description	Purpose
Calibration check (analytical balance)	Check the calibration of the analytical balance with Class S or better weight.	Assures that the analytical balance is in good working order.
Calibration curve	Verify instrumentation is working using traceable stock standard solutions. The supplier of this standard must be different from the supplier for the check standard.	Assures that equipment response is linear or curvilinear as expected and establishes the relationship between the instrument reading and the media concentration.
Blank	Test a blank made from deionized (reagent) water.	Identifies contamination from reagent water.
Calibration (check) standard	Test analyte content in a check standard prepared from a stock standard solution. Prepare standard solution from ACS-grade or NIST-traceable reagents.	Assesses accuracy and precision. Analyte recovery should be within 95% to 105%.
Laboratory replicates	Analyze sample in duplicate or triplicate.	Provides an on-going check of method precision.
Matrix spike	Add a known amount of analyte to sample media and take media through measurement. Determine the recovery of the spiked analyte.	Checks for matrix interferences. Analyte recovery should be within 85% to 115%, unless historical data indicate tighter limits can be routinely maintained.
Laboratory control sample	Internal media of known analyte concentration that is taken through the entire measurement process.	Assesses method accuracy and precision and is used to calculate method LOD. Serves as a method blank to identify contamination from reagents, glassware, and materials handling.
Independent or standard reference material	External media of known analyte concentration, preferably a media that has been tested by several laboratories, that is taken through the entire measurement process.	Assesses method accuracy and precision. Identifies systematic errors. Precision and recovery should not be statistically different that the certified value.

2.2.5 Other QA/QC activities

Operator (technician) training and method oversight through independent audits are two more QA/QC activities to serve not only reduce systematic error in test results but also to avoid costly rework that stem from such error. Operator training has many forms: demonstrations versus practice, one-on-one in the laboratory versus a classroom lecture, and in favor today internet-accessible video clips, webinars, and cartoons. For potentially life-threatening situations such as hazardous materials handling, training may be required on a recurring basis. Certification represents a formal documentation of a training program that was successfully completed. Independent audits of standard methods not only provide oversight on method performance, but put the method and operator in its proper context, a context that includes environmental influences (temperature, noise, dust, crowding), laboratory practices, and pressure for time. With competent auditors, independent audits are an excellent way to maintain method performance through time and across laboratories.

3 Measurement of Soil pH, Minimum Resistivity, Chloride, and Sulfate

3.1 Overview

The FMs for pH, minimum resistivity, chloride and sulfate were reviewed and compared with AASHTO, ASTM, and USEPA standard methods (Table 3-1). Theory of measurement for each method was also discussed to introduce interferences associated with the test methods and to identify method steps that have large leverage in test results.

Table 3-1 Selected Test Methods for Soil Electrochemical Properties

Agency	pH	Min Resistivity	Chloride	Sulfate
FDOT	FM5-550	FM5-551	FM5-552	FM5-553
AASHTO	T289	T288	T291A	T290B
ASTM	G51	G187	D512B	C1580
USEPA	Method 9045D	--	Method 9253	Method 9038

3.2 FM for pH

3.2.1 Theory of measurement

3.2.1.1 Acidity, activity, and ionic strength

The difference between soil acidity and pH, the basis of potentiometric measurements of pH, and the design of a typical pH measurement system were reviewed to understand the sources and nature of errors associated with electrochemical measurement of soil pH. To discuss soil acidity, a broad definition of an acid is needed. An acid is defined as a substance that when dissolved in water increases the concentrations of protons (H^+, or more accurately H_3O^+), or that donates H^+ to a chemical reaction, or that can accept an electron pair for a covalent bond (Snoeyink and Jenkins, 1980). Soils may contain not only strong mineral acids such as hydrochloric, nitric, and sulfuric acids, but also weak acids such as alcohols and amines, organic acids, and ferric (Fe^{3+}) or aluminum (Al^{3+}) ions. Titration of a soil extract yields a higher acidity than does an electrochemical measurement of pH, as the titration includes exchangeable H^+ that are made available as pH increases with titration, while an electrochemical measurement is sensitive to the H^+ activity at the soil pH. Soil pH is "the H^+ activity in the system when the solid and liquid phases are in equilibrium" (Peech and Bradfield, 1948), where $pH = -\log\{H^+\}$ and the relationship of H^+ activity (unitless) to concentration is $\{H^+\} = \gamma[H^+]$, the H^+ concentration is in molarity M (moles/liter) and the activity coefficient γ is in liters/mole. Activity represents the influence of charged ions or particles in solution on the analyte of interest. The activity coefficient γ is related in part to the ionic strength of the solution, which in turn is related to the concentration and valence of dissolved ions. In an aqueous extract of soil where the solution composition is unknown, solution conductivity (up to ~1,200 µS/cm) is a useful surrogate for ionic strength. For a solution conductivity less than ~100 µS/cm (resistivity greater than 10,000 ohm-cm), ionic strength is less than ~0.001 and γ for H^+ can be approximated as 1; such a solution is a low ionic strength solution.

3.2.1.2 pH measurement system and electrode design

At the core of the electrochemical pH measurement is the simplified Nernst equation (Equations 3-1 and 3-2), which applies to the change in free energy of a substance between two states, for example, its current state and a standard state, where E and E^0 are the current and standard state voltages (V), T is the temperature (K), R is the gas constant (C·V/mole·K), n is the number of electrons transferred in a reaction, F is Faraday's constant (C/mole), and 2.303 a conversion from the natural (ln) to base 10 logarithm (log) scales (Kohlmann, 2003). (In these simplified equations, the initial state voltage E^0 includes the reference electrode voltage.)

$$E = E^0 + \frac{2.303RT}{nF} log\{H^+\} \tag{3-1}$$

$$E = E^o - 0.059pH \quad @\ 25\ ^oC \tag{3-2}$$

The electrochemical pH measurement system consists minimally of two solution half-cells that are joined through a high impedance voltmeter and also by the sample across an H^+-sensing surface, for example, a glass bulb on the indicating cell, and a liquid junction on the reference cell (Figure 3-1). Ideally, in this system changes in voltage E are in response only to the $\{H^+\}$ of the sample, with all other system voltages E^o held constant. A silver/silver chloride reference electrode combined in one unit with an H^+-sensing glass membrane is commonly used in the laboratory. As an example design, the reference electrode consists of a silver wire with it terminus coated in silver chloride suspended in silver-saturated 4 M KCl. The half-cell reaction is silver chloride (solid) + e^- ↔ silver (solid) + chloride (aqueous). The indicating electrode has a silver wire coated with silver chloride that extends into the thin-walled glass bulb terminus, which is filled with 0.1 M hydrochloric acid solution. The half-cell reaction is silver (solid) ↔ silver chloride (solid) + e^-. The activity of protons adsorbed to the inside the glass bulb is fixed, but the protons adsorbed to the outside of the glass bulb depend upon the sample $\{H^+\}$ or pH. Adsorption and desorption of H^+ occurs in a thin (0.001 mm) hydrated gel layer on the glass bulb outer surface. At pH < 7.00, H^+ ions move into the gel layer; at pH > 7.00, H^+ ions move out of the gel layer. A change in H^+ between the inside and outside gel layers of the glass bulb creates a differential voltage (galvanic potential), which induces electron flow. Electron flow through the voltmeter produces a voltage drop proportional to $\{H^+\}$ in the sample; ion flow through the liquid junction maintains solution electro-neutrality. The total voltage measured by the pH meter includes the net voltages from the glass bulb interface, the electrolyte and wire of the indicating electrode, the electrolyte and wire of the reference electrode, and diffusion potentials at solid/solution (liquid junction) interface. Ideally, when measuring a pH 7.00 solution, these voltages sum to zero; in practice, the voltages do not sum to zero and the voltage displacement must be offset during calibration. The magnitude of the offset voltage (asymmetry potential) grows over time with the deterioration of either the indicating or reference electrodes.

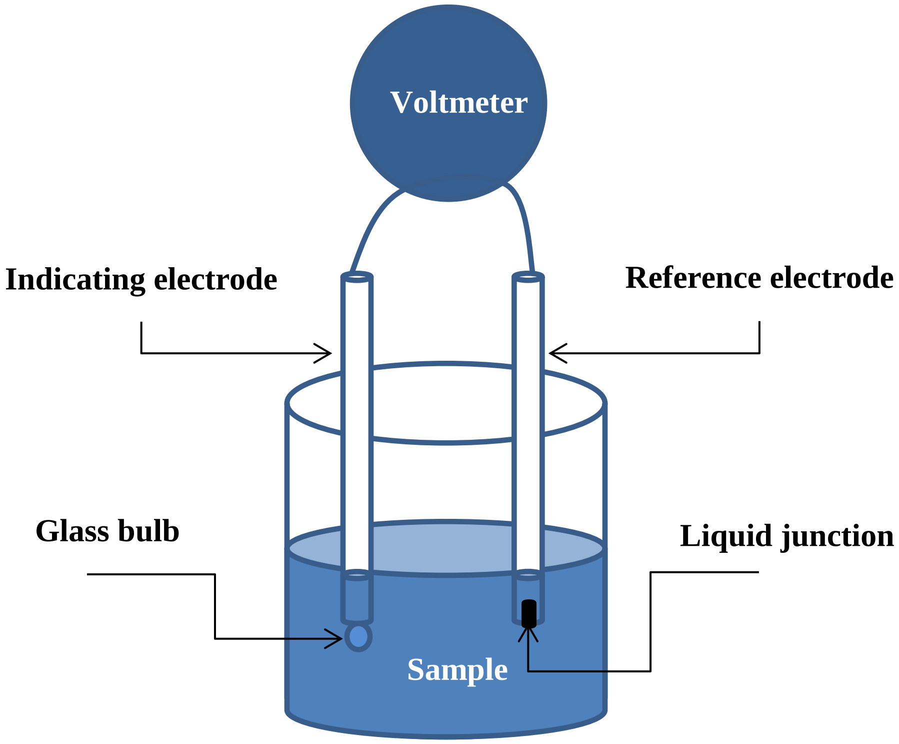


Figure 3-1. Schematic of a pH measurement system.

3.2.1.3 Liquid junction

A key component of the typical reference electrode design is the liquid junction. The purpose of this junction is to allow a small but steady leakage of the electrolyte into the sample solution during the measurement process so as to provide ion flow to maintain solution electro-neutrality. Many combination electrodes allow the reference electrode electrolyte to be replenished over time. Junctions are commonly made of a non-reactive porous material such as ceramic or fiber; the number and geometry of the junctions vary with the pH measurement application. An equi-transferent electrolyte at high ionic strength such as 4 M potassium chloride keeps low the voltage drop across the liquid junction (Brezinski, 1985; Kadis and Lieto, 2010). Equi-transferent for potassium chloride means that both the potassium and chloride ions diffuse at roughly the same rates, which evenly distributes the charge through the liquid junction. The flow rate of the electrolyte through the liquid junction dictates the responsiveness—stability and speed—of the electrode (Davison and Woof, 1985). For routine pH measurements in low ionic strength waters, a liquid junction designed for a higher electrolyte flow rate is recommended (Davison and Woof, 1985; Illingworth, 1981). A double-junction electrode is better suited for dirty samples. In a double-junction electrode the potassium chloride electrolyte that contains silver chloride is retained by the first junction in a chamber containing the wire, and a potassium chloride electrolyte (with trace silver chloride) is retained by the second junction in an adjoining chamber, where the second junction bridges the electrolyte and the sample. This design reduces contamination of the first junction and chamber by the sample.

3.2.1.4 Temperature error

The temperature-dependence of pH measurements has at least three sources: (1) the electrochemical reaction as expressed by the Nernst equation, (2) the change in resistance of the glass used in the H^+-sensing glass bulb, and (3) the dissociation of ions in solution. From Equation 3-1, pH measurement is sensitive to temperature. The contribution of this error to the total temperature error is 0.003 pH error/ΔpH unit/Δ°C, where ΔpH unit and Δ°C are referenced to pH 7 and 25°C, respectively, or ~0.05 pH units for a sample solution at pH 4.00 and 30 °C. Glass resistivity decreases with increasing temperature, which changes the voltage drop across the glass and thus the measured pH. The relationship of glass resistance to temperature depends on the type of glass, its size, shape, and thickness, and the condition of hydrated layer. Modern instruments automatically compensate for the shift in voltage due to a change in glass resistance provided that the solution temperature is either sensed by the electrode or otherwise measured and input into the pH meter. Finally, the dissociation of ions in solution is temperature-dependent. For example, in pure water at 25 °C, 10^{-7} moles/liter of H_2O disassociates into H^+ and OH^-; more water dissociates at higher temperatures and less at lower temperatures; thus, at 20°C, pH 7.08 is neutral and pH 7.00 is acidic (Table 3-2) (Skoog et al., 1996). The temperature of the sample affects the H^+ concentration on both sides of the glass bulb, but the net effect will depend on sample composition. The temperature effects on pH measurements highlight the importance of measuring calibration buffer and samples at the same temperature and at or near 25 °C.

Table 3-2 Influence of Temperature on the pH of Pure Water

Temperature (°C)	pH
10	7.27
20	7.08
25	7.00
30	6.92
40	6.77

3.2.1.5 Sodium (alkaline) and acid errors

Sodium ions if present in the sample at much greater concentrations than H^+ ions can penetrate into the glass and displace H^+ ions with a commensurate shift the charge balance. The actual conditions under which the shift occurs depends upon electrode design, temperature, and precedent exposure, but may be significant at pH >11. Under extremely acidic conditions (pH < 1), the high acid content relative to water content diminishes the gel layer thickness; the consequence is a higher measured versus actual pH.

3.2.1.6 Soil-to-water ratios

Soil-to-water ratios used for pH measurement vary widely, for example, from a saturated paste to dilutions of 1:5; a 1:1 soil-to-water ratio using distilled or deionized water is typical (Miller and Kissel, 2010). Miller and Kissel (2010) found that pH increased with water dilution. For their dataset of North American soils, the non-linear increase was from pH 4.50 for a saturated paste to pH 4.87 for a 1:1 soil-to-water dilution to pH 5.62 for a 1:5 soil-to-water dilution. Puri and Asghar (1938) proposed that salt present in soils depressed the soil pH. Their experimental work was with soils leached free of base cations, to which select base cations were added at soil-to-water dilutions of 1:5 to 1:25. They found that in the absence of base cations, the soil pH did not change with water dilution; in the presence of even small amounts of added neutral salts, however, the pH decreased. Conversely, leached soils had a higher pH than their unleached counterparts, but leached and unleached soils extracted in potassium chloride had the same pH. Their explanations for these phenomena were that (1) the presence of a salt reduced the hydrolysis of an exchangeable base, and (2) surface ionization of colloidal particles was not affected by dilution. In other words, adding water to the soil diluted the soil's salt content, which raised the pH. Puri and Asghar (1938) recommended that soils be extracted in a potassium chloride solution to assure uniformity in pH results.

3.2.1.7 Stirring error

A difference in pH is sometimes observed between a stirred and quiescent solution, and this difference is termed a stirring error. Brezinski (1983) reported that the root cause of the stirring error was a change in the electrode electrolyte concentration (e.g., 4 M potassium chloride) at the interface of the liquid junction and the sample. Errors were minimal for a well-designed electrode when the sample was similar in ionic strength and transference to the electrolyte, for example, with standard buffers used to calibrate pH electrodes. He postulated that for dissimilar solutions, mixing of sample solution and electrolyte solution occurred within the liquid junction and caused a shift in voltage drop. Moreover, between two dissimilar samples the liquid junction "remembered" the last sample (consistent with a trace of the last sample retained in the liquid junction), and this effect—while transient—significantly slowed the electrode response. For example, Brezinski (1983) found that transferring an electrode from a 1 M potassium chloride to a 10^{-4} M hydrochloric acid sample resulted in a relatively stable pH reading that was -0.6 pH units in error. Stirring effects were exacerbated for no-flow (non-refillable gel electrodes) or low-flow (i.e., clogged) electrodes, and for low-ionic strength samples. Davison and Woof (1985) recommended monitoring the stirring error as a measure of electrode performance and stated that for low ionic strength solutions, pH measured without stirring were closest to the expected pH.

3.2.1.8 Ionic strength

An electrochemical pH measurement is a challenge in low ionic strength solutions. In pure water that is equilibrated with carbon dioxide at atmospheric concentrations, the addition of a neutral salt such as 1 M potassium chloride can shift the pH downward by ~0.10 pH units due to the dissimilarities in ionic strength and transference between the electrolyte and sample (Bier, 2009; Brezinksi, 1983; Kadis and Leito, 2010). Illingworth (1981) reported a 0.2 pH unit error for each 10-fold difference in salt concentration between the calibration buffer and an aqueous sample. Increasing the ionic strength of the pure water sample improves the stability and speed of the pH measurement (Bier, 2009). In 1:1 soil-to-water extracts of soil, however, the addition of a neutral salt such as 1 M potassium chloride or 0.01 M calcium chloride causes a shift in pH of ~0.5 pH units (Miller and Kissel, 2010) to 2 pH units (Peech and Bradfield, 1948; Yuan, 1963), and explanations for this shift were more complicated. In the agricultural sector, amendment of samples with 0.01 M calcium chloride is often recommended not only to reduce the sensitivity of pH measurement to salt concentration in low ionic strength solutions but also to better estimate lime requirements in the presence of a seasonal change in soil pH measurements due to rainwater leaching of salts of agricultural soils (Kissel et al., 2009).

Statistical models have been developed to relate the pH of 1:1 soil-to-water extracts with that of 1:1 soil-to-0.01 M calcium chloride extracts, as these pH values are strongly correlated (Brennan and Bolland, 1998; Miller and Kissel, 2010; Minasny et al., 2011). The observed downward shift in pH with the addition of neutral salts to soil extracts is due to a combination of factors that include the displacement by added metal cations (potassium, calcium) of (1) exchangeable H^+ and (2) exchangeable aluminum, iron, and manganese, which may be subsequently hydrolyzed and act as H^+ sources, and (3) the presence of a voltage bias at the liquid junction due to the difference ionic strength between the electrode electrolyte and soil extract (Miller and Kissel, 2010; Peech and Bradfield, 1948;Yuan, 1963). Miller and Kissel (2010) argue that because the downward shift in pH is relatively constant for both acid and alkaline soils, the voltage bias at the liquid junction dominates the effect. Miller and Kissel (2010) made an argument for extracting a soil with a neutral salt solution but Busenberg and Plummer (1987) argued the opposite because of the potential for pH-altering contamination in purchased salts.

3.2.1.9 Carbonate Equilibria

Measurement systems for pH can be open or closed; closed systems are more often found in process monitoring than on a laboratory bench. In an open system such as a 1:1 soil-to-water suspension in an open beaker, solution and atmospheric gases will exchange and trend to equilibrium at the solution pH, temperature, ionic strength, and with stirring. Carbon dioxide is present in the atmosphere at an average global concentration approaching 400 ppm; local atmospheres (urban and laboratory as examples) and *in situ* soils may see higher carbon dioxide concentrations (Macpherson, 2009; Rice and Bostrom, 2011). At a room temperature of 25 ^oC, a stirred beaker of pure water tends towards a carbonate equilibrium of pH 5.6 or an $\{H^+\}$ of 2.5×10^{-6} M. The interference of carbon dioxide on pH measurements on soil pH will be the greatest for a near-neutral, low ionic strength soil with little buffering capacity (Figure 3-2). In this case, similar to pure water, the pH electrode response will be slow, noisy, and unstable, and with significant stirring effects.

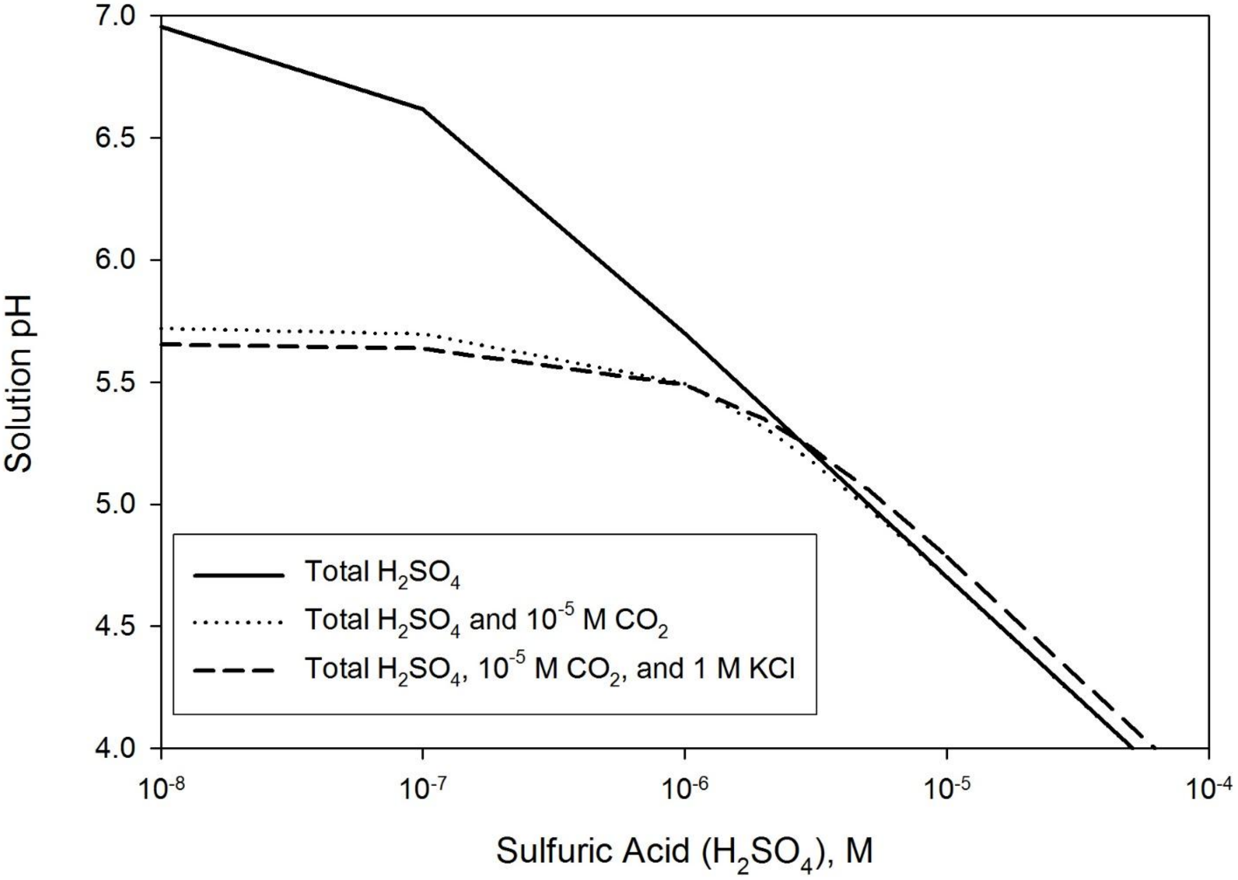


Figure 3-2. Calculated influence of carbon dioxide on an open-system pH measurement of a weak sulfuric acid solution with and without KCl added.

3.2.1.10 Suspension error

Suspended colloidal particles—particles in the size range of 0.001 to 0.10 µm—interfere with electrochemical pH measurements (Keller and Matlack, 1990; Yang et al., 1989). Literature defined the suspension effect in two ways: (1) the change in measured pH with the addition of suspended particles, and (2) the change in pH for indicating and reference electrodes immersed in the sediment suspension versus both electrodes immersed in a solution equilibrated with the sediment. Colloidal particles are difficult to filter or settle and if present in the soil will be suspended in the soil extract. Keller and Matlack (1990) wrote that pH paper worked better than electrochemical measurement for determining pH in clay soils, even after the soil extract was filtered through a 0.10 µm filter to produce an optically-clear solution. Yang (1989) and Oman (2000) agreed that the suspension effect is the combined response of the indicating and reference electrodes to particles suspended in the sample. In general, the charge fields of indicating electrode and particles proximate to or adsorbed on the indicating electrode interact to alter the electrode voltage. Moreover, the electrolyte effusing from the reference electrode liquid junction interacts with suspended particles to create an ‘anomalous liquid junction potential.’

3.2.1.11 Damage to the electrode

A pH electrode is a fragile and sensitive instrument and is easily damaged. Rough handling or abrasive samples can break or crack the glass bulb. An unresponsive reading, usually a pH 7.00 or 0 mV reading in all buffers and samples, is a symptom of a broken glass bulb or wire. This may go undiagnosed if the electrode is calibrated with only a pH 7.00 buffer. Colloidal particles suspended in soil extracts can migrate into and clog the liquid junction as can silver chloride or insoluble silver precipitates. A slow electrode response or steep stirring potentials indicate a clogged liquid junction. Colloidal particles or dissolved sample constituents can migrate through the liquid junction and into the electrolyte when the height of the sample is above the height of electrolyte, as evidenced by a change in the electrolyte opacity or color or electrode performance. A dry glass bulb affects electrode response. Proper hydration of the glass bulb is necessary for a stable reading; storage in distilled or deionized water can deplete the hydrated gel layer. Oil, enzymes, or particles adhered to the glass bulb affect electrode performance but can be removed with an appropriate cleaner. Many but not all of these adverse effects can be reversed with proper electrode maintenance.

3.2.2 Description of method

FDOT specifies FM 5-550 for testing the pH of soil in candidate MSE wall backfill material (Chapter 2, Section 2.1.2). As presented in Section 3.2.1, the basis of this measurement is a potentiometric measurement using an indicating electrode and a reference electrode, where the voltage produced in this system is linear with pH. The voltage response to pH is calibrated with buffers of known pH at the measured sample temperature.

The first step towards analysis of pH in soil is preparation of the soil sample. Per the FM, these steps are:

- Place 100 mL of soil sample in a beaker and add an equal volume of distilled or deionized (dilution) water;
- Break any soil clumps and stir the mixture at 10 min intervals for 30 min;
- Allow sample to reach room temperature;
- Calibrate the pH meter and electrode every 30 min or if a difference of one pH unit is encountered between tests; and
- Calibrate with a standard buffered solution in the range of the sample to be tested or with a pH 7 standard buffer if the sample pH is not known.

The steps to measure pH in soil are given by either the manufacturer's instructions or by Standard Methods for the Examination of Water and Wastewater (SMEWW) 4500-H^+ B (Rice et al., 2012). Typical steps are:

- Set meter mode to pH;
- Rinse the pH electrode with distilled water;
- Dip the pH electrode and temperature sensor into the sample;
- Allow time for the reading to stabilize; and
- Record the pH reading.

SMEWW 4500-H^+ B recommends that the pH meter be re-calibrated if the buffer solution pH after calibration measures more than 0.1 pH unit from its expected value, which may indicate a faulty electrode.

3.2.3 Method comparisons

3.2.3.1 Soil processing

The FM for pH requires that the soil be transported in a cool dark area and if stored, stored at 4°C for no more than seven days. Soil is tested in the "as received" condition. Per AASHTO T289 soil is selected according to AASHTO T248, dried to a moist condition either in air or in a drying apparatus not to exceed 60°C (which AASHTO T289 states is equivalent to air drying), and sieved with a 2.00-mm (No. 10) sieve. ASTM G51 is for *in situ* field measurements of pH. Calibration of the pH meter is generally consistent with other methods discussed herein; however, the pH electrode is lowered into the surface or subsurface through an augured hole to make direct, undiluted contact with the soil (with the caveat that some soils may be too dry). The pH electrode can be installed in a protective casing for ease of handling.

3.2.3.2 pH meter and electrode calibration

For pH meter calibration, the FM calls for use of at least one standard buffer solution in the range of the pH to be tested or pH 7 if the range is unknown; AASHTO T289 and USEPA 9045D use at least two buffer solutions that are 3 pH units apart and bracket the sample pH. Re-calibration is required after every 30 min or if a difference in one pH unit is encountered; both of these methods require temperature compensation, but with USEPA 9045D, after calibration the measured buffer pH should be within 0.05 pH units of the stated value.

3.2.3.3 Soil testing

The FM for pH calls for 100 mL of "as received" soil, an amount that for moist sand typically weighs from 150 to 170 g, to which is added 100 mL of dilution water. AASHTO T289 specifies

30 g of soil and to which is added an equal mass of dilution water. With the FM for pH, soil and water are equilibrated for 30 min with stirring at 10-min intervals; for AASHTO T289 soil and water are equilibrated for 60 min with stirring at 10-min intervals. For USEPA 9045D, soil with less than 20% moisture is tested; 20 mL of dilution water is added to 20 g of soil, and the slurry is continuously stirred for 5 min and allowed to settle for 1 hr. The water portion of the slurry is then decanted, filtered, or centrifuged to separate the water from clay particles before its pH is measured. In short, for these three methods the soil is either "as received" or dried and sieved, with soil-to-water ratios between 1:1 and ~1.5, sample sizes from 20 to 150 g, and sample extracts either filtered or unfiltered. SMEWW 4500-H^+ B recommends that for dilute, poorly buffered samples, the pH electrode be equilibrated with three to four successive portions of the sample. SMEWW 4500-H^+ B and USEPA 9045D both mention that a sodium error is likely at pH >10, in which case a low-sodium error electrode should be used. Another variation on soil pH measurements is to use a 0.01 M calcium chloride (Miller and Kissel, 2010; ASTM D4972) solution in lieu of distilled or deionized water. According to ASTM D4972, the added calcium displaces exchangeable aluminum in the soil and the elevated salt content better represents the *in-situ* soil ionic strength.

3.2.4 Estimate of method precision and bias

According to Fisher Scientific (2012), for an AB150 benchtop meter, the pH range is -2.000 to 20.000 pH, with a resolution of 0.001 pH units and an accuracy of ± 0.002 + 1 LSD pH units (LSD is not defined in the manual). For SMEWW 4500-H^+ B method precision and accuracy are ±0.02 pH and ±0.1 pH, respectively, under normal conditions for water and poorly buffered solutions (Rice et al., 2012).

3.3 Minimum Resistivity

3.3.1 Theory of measurement

Soils with a higher concentration of salts are more corrosive. A measure of a soil's salt content is resistivity, where salt content is inversely proportional to resistivity. Soil resistivity measurements can be made *in-situ* or on a laboratory bench and while the latter approach of interest here, equipment design (Section 3.3.2) likely evolved from field techniques. Ohm's Law relates resistance R to voltage V and current I, where $R = V/I$ in compatible units. In concept, impressing I across a block of soil generates a V, which is measured and from which R is calculated. Resistance R is a property of the soil block; to express as a property of the soil, R in ohms is converted to resistivity ρ in ohm-cm according to the geometry of the block and Equation 3-3 (Samouëlian et al., 2005):

$$\rho = R\frac{Area}{Length} \tag{3-3}$$

Resistance of a soil to its conduct of ions depends upon its liquids, solids, and voids (Samouëlian et al., 2005). Water content, amount and type of dissolved ions, and the presence of other fluids such as oil affect soil resistivity. For example, as water content in soil is increased from near zero to 15%, a soil's resistivity rapidly decreases, as illustrated in Figure 3-3 for sands from Mines 5 through 8 (Chapter 1, Section 1.2.7, Table 1-1). Resistivity is also affected by a soil's mineral composition and particle size distribution and tends to decrease with an increase in clay content, as clay particles have a high surface charge density. Finally, the number, size, and connectivity of voids in a soil's matrix affect the movement of ions through a soil and thus its resistivity. These same soil constituents—liquids, solids, and voids—have insulating or dielectric properties that respond to the frequency of the applied current (White and Zegelin, 1995). The ability to differentiate the earth's subsurface features by varying the frequency of applied current has led to advances in electrical prospecting, environmental surveys, and water content mapping (White and Zegelin, 1995).

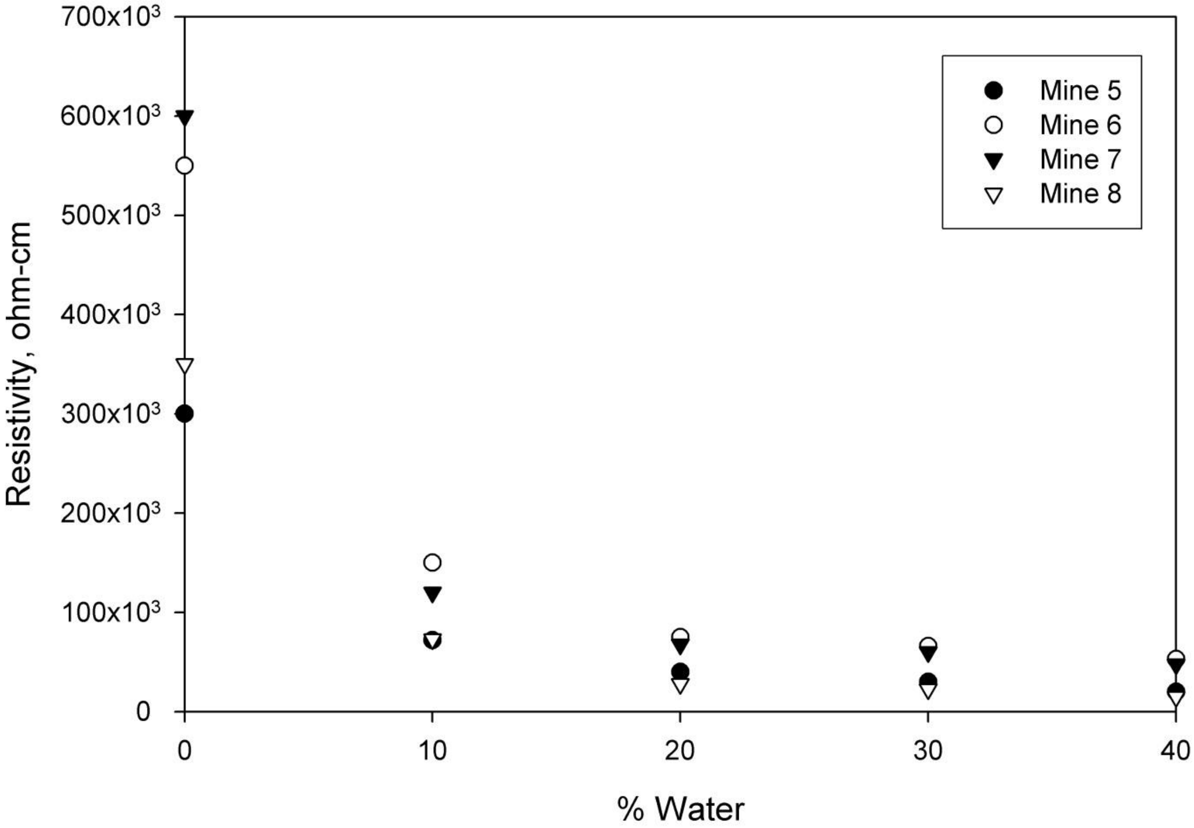


Figure 3-3. Resistivity versus water content for sands from mines 5 through 8.

Ion motion increases with temperature, thus soil resistivity decreases as temperature increases. ASTM G187 requires that laboratory measurements be made at or near 20°C, but offers Equation 3-4 to correct resistance at field temperature R_T to resistance at a standard temperature of 15.5°C $R_{15.5}$, where T is the field temperature in °C.

$$R_{15.5} = R_T(24.5 + T)/40 \tag{3-4}$$

For similar soil resistivity meters (Miller 400A, Nilsson 400, and Tinker and Rasor SR-2, as examples), an alternating current at ~97 Hz is applied to pins C_1 and C_2 of a four-pin soil box and the voltage drop is measured between pins P_1 and P_2 (Figure 3-4). A two-pin measurement is possible with the voltage drop measured between pins C_1 and C_2; the four-pin configuration, however, eliminates the problem of contact resistance at the electrodes (White and Zegelin, 1995). The soil resistance in ohms is read from the meter and multiplied by the geometry-dependent distance (cm) between P_1 and P_2 to get resistivity (ohm-cm). The FM for minimum resistivity calls for a soil box area-to-length ratio of 1 cm. AASHTO T288 and ASTM G157 both use a two-pin measurement and provide guidance for construction of soil box and calculation of the area-to-length ratio based on the box geometry.

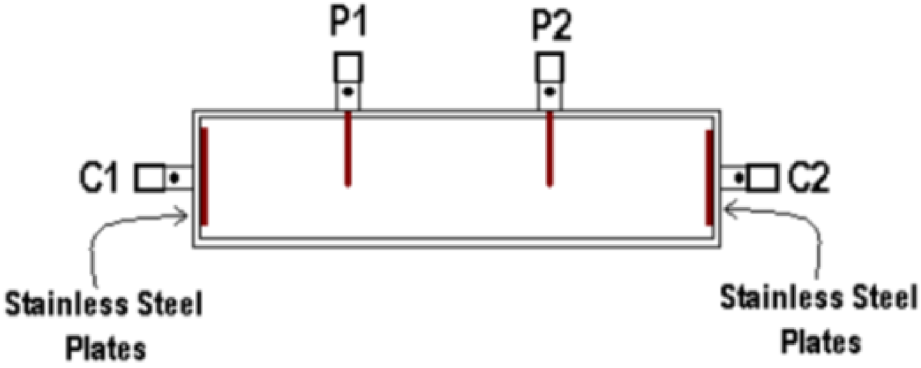


Figure 3-4. Diagram of soil box for measurement of soil resistivity.

3.3.2 Description of method

FDOT specifies FM 5-551 for testing the minimum resistivity of soil in candidate MSE wall backfill material (Chapter 2, Section 2.1.2). As presented in Section 3.3.1, soil resistivity is based on a measured voltage drop due to an impressed current across wetted soil that is contained in a box of standard dimensions.

According to the FM for minimum resistivity, the method steps are:

- Rinse the soil box with deionized water before and after completion of each test;
- Follow the manufacturer’s instructions for connecting the leads to the soil box;
- Place one kg of as-received soil sample in a large round pan; remove debris and mix soil sample;

- Fill the soil box, compact, and level; connect the soil box to the meter and determine the resistance; place the soil sample back into the pan;
- Record the volume of water used and the corresponding resistance reading;
- Add 100 mL of distilled/deionized water to the soil sample, mix thoroughly, and repeat the above procedure until the lowest resistance is obtained; and
- Report results of minimum resistivity with units of ohm-cm.

3.3.3 Methods comparisons

3.3.3.1 Soil processing

The FM for minimum resistivity does not require that the soil be dried or sieved, nor are soil storage instructions provided. AASHTO T288 requires that the soil sample is dried in air or in a drying apparatus not to exceed 60°C, and that the sample is selected per AASHTO T248 and sieved with a 2.00-mm (No. 10) sieve, such that 1,500 g is available for the test. Moreover, 150 mL of dilution water is added to the 1,500-g sample of dried soil and the wetted sample is covered and allowed to equilibrate or cured for a minimum of 12 hr. Dilution water must have a resistivity greater than 20,000 ohm-cm. ASTM G187 does not require either drying or sieving of the soil sample, but requires laboratory testing at room temperature and cautions against field-testing soils that are frozen or partially frozen, and gives an equation to convert resistances measured in the field to a standard temperature of 15.5°C (Equation 3-4). Dilution water must have a resistivity greater than 200,000 ohm-cm.

3.3.3.2 Method calibration

Calibration of the soil resistivity meter is established by checking the zero of the meter, verifying the resistance of resistors across a range of known values, and measuring the resistivity of standard salt solutions. The FM for minimum resistivity does not include a calibration step, but AASHTO T288 requires calibration of the soil resistivity meter with 100-, 200-, 500- and 900-ohm resistors; the meter readings must be within 10% of the resistor value. ASTM G187 recommends (1) periodically calibrating the soil resistivity meter with a commercial resistance decade box or with a series of resistors of different values; the meter errors must be within 5% over the range of the instrument, and (2) twice a year checking the meter and box with standard solutions in the range of 1,000, 5,000, and 10,000 ohm-cm.

3.3.3.3 Soil testing

Steps for soil testing in the FM for minimum resistivity are nearly identical to those for AASHTO T288, with one important exception. For AASHTO T288, as water is added and soil slurry develops, the method operator is directed to fill the soil box with slurry water first, and if the water cannot fill the box to the top, to continue to fill the box with slurry soil. Thus, the minimum resistivity may occur when the box is completely full of slurry water. ASTM G187 measures soil resistivity when the soil is just saturated with water. Soil is placed in the box layer by layer, and each layer is wetted and then densely compacted by hand. When the box is full and leveled, a thin sheen of water is present on the soil surface. The resistivity of soil at water saturation is not the same as minimum resistivity.

3.3.4 Estimate of method precision and bias

The resistance meter's range is typically 0.01 ohm to 1,100,000 ohm, and the accuracy of the measurement is ± 10% at full scale and ± 5% at 85% of full scale (Corrpro, 2013; MCM, 2011; Tinker and Rasor, 2013). ASTM G187 reported the results for a 2003 inter-laboratory study in Tampa, Florida: across three soils the reproducibility was 10.6%; therefore at the 95% confidence level, results of two properly-conducted tests in different laboratories on the same material were not expected to differ by more than 29.7%.

3.4 Chloride

3.4.1 Theory of measurement

The basis of the wet chemistry chloride test is the titration of dissolved chloride with silver nitrate to form relatively insoluble silver chloride in neutral or slightly alkaline solution. The titration endpoint is indicated by the reaction of potassium chromate with unreacted silver to form red silver chromate. According to Rice et al. (2012), sulfide, thiosulfate, and sulfite ions can interfere but can be oxidized by treatment with hydrogen peroxide. Elevated levels of orthophosphate or iron may also interfere. Bromide, iodide, and cyanide titrate as chloride. With soil extracts, the presence of color and suspended particles interfere with diagnosis of the titration endpoint. The measurement range is 5 to 250 ppm chloride and stated range varies with method, or more specifically, with the volume of sample (mg of chloride) and concentration of silver nitrate. The advantages of this test are its relative simplicity, portability, speed, and low cost; its disadvantages are interferences from suspended soil particles and the use of hazardous materials including silver nitrate and potassium chromate. Other methods for water-soluble chloride include titration with mercuric nitrate, detection of chloride ions with an ion-specific electrode, and ion chromatography, in order of increasing equipment cost and complexity.

3.4.2 Description of method

FDOT specifies FM 5-552 for testing water-soluble chloride in candidate MSE wall backfill (Chapter 2). The sample analysis steps in the FM for chloride are determined either by Hach method 8207 (Hach, 2003) or by Standard Methods for the Examination of Water and Wastewater (SMEWW) 4500-Cl^- B, argentometric method (Rice et al., 2012).

The first step towards analysis of chloride is preparation of the soil sample. Per the FM, these steps are:

- Dry sample to constant mass for ~four hr in an oven at 110°C;
- Sieve through a No. 10 (2.0 mm) mesh sieve; and
- Split the sample per AASHTO T248 (ASTM C702) to obtain ~400 g.

The second step towards analysis is an aqueous extraction of chloride from soil. Per the FM, these steps are:

- Combine in a 500-mL flask 300 mL of water with 100 g of dried soil;
- Shake mixture for 20 s, then allow to settle for one hr and shake for another 20 s;
- Settle the soil suspension for a minimum of 12 hr;
- Gravity filter through a fast, coarse filter the soil suspension to produce a clear extract; and
- Allow the test sample to reach room temperature.

The sample analysis steps for Hach 8207 are as follows:

- Select the appropriate silver nitrate cartridge (concentration);
- Insert a clean delivery tube into the titration cartridge and attach the cartridge to the digital titrator;
- Hold the digital titrator with the cartridge tip pointing up, turn the delivery knob until a few drops of titrant are expelled, then reset the counter to zero;
- Use a graduated cylinder or pipet to measure sample volume and bring volume up to 100 mL;
- Transfer sample to a clean 250-mL flask;
- Add the contents of one Chloride 2 (potassium dichromate and sodium bicarbonate) indicator powder pillow and swirl to mix;
- Place delivery tube tip into the sample solution and swirl the flask while titrating with silver nitrate from a yellow to a red-brown color;
- Record the number of digits required;
- Calculate the soil chloride concentration from the number of digits, multiplication factor, and dilution factor; and
- Report chloride results in ppm.

SMEWW 4500-Cl^- B is very similar to Hach 8207. Both of these methods note that samples should be adjusted to a near neutral pH with sulfuric acid or sodium hydroxide and treated with hydrogen peroxide to remove sulfite interference; however, SMEWW 4500-Cl^- B recommends treating the sample with an aluminum hydroxide suspension if sample is highly colored.

3.4.3 Method comparisons

3.4.3.1 Soil processing

ASTM D512B and USEPA 9253 methods assume water samples and thus give no guidance on soil processing. For AASHTO T291A, soil samples are dried in air or in a drying apparatus not to exceed 60°C, soil is sieved through a No. 10 (2 mm) mesh, and a 250-mg sample is selected based on AASHTO T248. With the lower drying temperature, some moisture is retained in the soil. AASHTO T291A has as a final step adjustment of the chloride concentration to the moisture content of a soil subsample dried to 110°C. For both the FM for chloride and AASHTO T291A, 100 g of soil is diluted with 300 mL of reagent water, shaken to mix, allowed to settle for one hr, and then shaken to mix once more. Reagent water is ASTM 1193 Type III, which has a minimum resistivity of 4,000,000 ohm-cm and a maximum chloride concentration of 0.010 ppm. The AASHTO T291A method separates without delay the suspended soil particles by centrifugation (50 mL centrifuge tubes), followed by filtration through a 0.45-µm filter if turbidity remains.

3.4.3.2 Method Calibration

For an accuracy check, Hach method 8207 recommends titrating increments of standard solution added directly to the sample; a linear response indicates no interference. Both SMEWW 4500-Cl^- B and AASHTO T291A include steps to standardize the silver nitrate titrant against a sodium chloride standard and to establish the reagent blank value, while ASTM D512B tests two levels of the same sample to screen for interferences.

3.4.3.3 Soil testing

USEPA 9253 and ASTM D512B are nearly identical. AASHTO T291 and ASTM D512B are similar to Hach method 8207 and SMEWW 4500-Cl^- B, but ASTM D512B has the below-listed key variations:

- Dilution water is ASTM D1193 Type IV, with a minimum resistivity of 200,000 ohm-cm and a maximum chloride concentration of 0.050 ppm;
- Use of a sample size less than 50 mL, diluted to 50 mL;
- Adjustment of the sample pH to the phenolphthalein endpoint of 8.3;
- Titration of the sample in a white porcelain dish;
- Sample testing under yellow light or with yellow goggles; and
- Repetition of the analysis with one-half the sample size to screen for interferences.

3.4.4 Estimate of method precision and bias

ASTM D512B reported the precision and bias results from an inter-laboratory study. Precision and bias were concentration-dependent. The reproducibility standard deviation was $s_R = 0.013X + 0.70$, where X is the chloride concentration; for an 80 ppm chloride concentration, s_R was 1.74 ppm; therefore at the 95% confidence level, results of two properly-conducted tests in different laboratories on the same material were not expected to differ by more than 4.9 ppm. For an 80 ppm chloride concentration, the method bias was -1.13 ppm.

3.5 Sulfate

3.5.1 Theory of measurement

FDOT specifies FM 5-553 for testing water-soluble sulfate in candidate MSE wall backfill material (Chapter 2, Section 2.1.2). The basis of the test is a reaction of barium chloride with dissolved sulfate to form relatively insoluble barium sulfate. The reaction is allowed to proceed for a few minutes, after which time the visible light absorption of barium sulfate precipitate is read with a photometer at ~450 nm and over a path length of 2 cm. The test range is 2 to 70 ppm, and minimum detection level is ~2 ppm. Interferences include sulfite and sulfides, which oxidize to sulfate, suspended particles, and color. The advantages of this test are its relative simplicity, portability, speed, and low cost; its disadvantages are interferences from suspended soil particles and use of a hazardous material barium chloride. Other methods for water-soluble sulfate include gravimetric, colorimetric, and ion chromatographic methods, in order of increasing equipment cost and complexity. The gravimetric and colorimetric methods also use barium chloride as a reagent. Hayes (2007) completed a comparison of four methods for water-soluble sulfate from soil extracts and recommended the ASTM C1580 gravimetric method over the ASTM C1580 turbidimetric method due to instrument drift. Hayes (2007) used a 2005 version of ASTM C1580; the 2009 version, however, does not include a gravimetric method.

3.5.2 Description of method

The sample analysis steps in the FM for sulfate are determined either by Hach method 8051 (Hach, 2012) or by Standard Methods for the Examination of Water and Wastewater (SMEWW) 4500-SO_4^{2-} E argentometric method (Rice et al., 2012). The first step towards analysis of sulfate in soil is preparation of the soil sample. Per the FM, these steps are:

- Dry sample to constant mass ~four hr in an oven at 110°C;
- Sieve through a No. 10 (2.0 mm) mesh sieve; and
- Split the sample per AASHTO T248 (ASTM C702) to obtain ~400 g.

The second step towards analysis of sulfate is an aqueous extraction of sulfate from soil. Per the FM, these steps are:

- Combine in a 500-mL flask 300 mL of water with 100 g of dried soil;
- Shake mixture for 20 s, then allow to settle for one hr and shake for another 20 s;
- Settle the soil suspension for a minimum of 12 hr:
- Gravity filter the soil suspension through a fast, coarse filter to produce a clear extract;
- Add hydrochloric acid to clarify the extract, if cloudy; and
- Allow the test sample to reach room temperature.

Both Hach Pocket Colorimeter II Analysis System for Sulfate (Hach sulfate) and Standard Methods for the Examination of Water and Wastewater (SMEWW) Method 4500-$SO_4^=$ E (Rice et al., 2012) are acceptable for the FM for sulfate. The procedure for Hach sulfate is:

- Fill a cell with 10 mL of filtered soil extract (sample);
- Add SulfaVer 4 reagent (powder of barium chloride and citric acid) to cell;
- Swirl vigorously to dissolve powder;
- React barium chloride in sample for 5 min;
- Prepare a blank containing sample but no SulfaVer 4 reagent;
- At the end of the 5-min reaction period, insert the blank in the photometer and zero the meter;
- Insert sample cell into photometer and read sulfate concentration in ppm (calibration curve is programmed into the photometer);
- Multiply the photometer value by the dilution factor to get the soil sulfate concentration; and
- Report the sulfate results in ppm.

SMEWW 4500-$SO_4^=$ E takes a different approach:

- Measure 100 mL of sample into a 250-mL flask;
- Add 20 mL of buffer solution and mix in a stirring apparatus at constant speed;
- Add a spoonful of barium chloride crystals and continue to stir for 60 ± 2 s;
- Pour solution into a reaction cell and measure light absorption at 5 ± 0.5 min;
- Subtract from this the light absorption for a sample blank containing no barium chloride;
- Determine the sulfate concentration from the calibration curve;
- Multiply the sample sulfate concentration by the dilution factor to get the soil sulfate concentration; and
- Report the sulfate results in ppm.

The buffer solution contains distilled water, magnesium chloride, sodium acetate, potassium nitrate, and acetic acid, and is intended to stabilize the barium chloride suspension.

3.5.3 Method comparisons

3.5.3.1 Soil processing

AASHTO T290B, ASTM C1580, and USEPA 9038 have the same basis as the FM for sulfate; USEPA 9038, however, assumes a water sample. In AASHTO T290B, the soil preparation procedure calls for drying the sample in air or in a drying apparatus not to exceed 60°C, selection of 250 g soil by AASHTO T248, and sieving through a No. 10 (2 mm) mesh. With the lower drying temperature some moisture is retained in the soil, and AASHTO T290B has as a final step adjustment of the sulfate concentration to the moisture content of a soil subsample dried to 110°C. ASTM C1580 requires drying 100 g of the sample at 60°C but for 18-24 hr, and crushing and sieving the sample through a No. 30 (0.60 mm) mesh.

AASHTO T290B mixes 300 mL of water and 100 g of soil but separates the suspended soil particles without delay by centrifugation, followed by filtration through a 0.45-µm filter if turbidity remains. No details are given on the centrifugation volume or speed. As with the FM for sulfate, a drop of concentrated acid is added as needed to precipitate any remaining finely divided suspended matter after centrifugation and filtration. ASTM C1580 mixes 3 g and 30 g of the soil each with 250 mL of dilution water; both samples are stirred for an hr and then filtered, twice if needed, to get a clear extract. Dilution water is ASTM D1193 Type I (18,000,000 ohm-cm).

3.5.3.2 Method calibration

Two sulfate calibration curves in the range of 0 to 70 ppm are pre-programmed in the photometer for the Hach sulfate method. One curve has a steeper slope than the other; the choice of curves may be needed to adjust for either the age or the manufacturer of barium chloride reagent, as is suggested by Figure 3-5. SMEWW 4500-$SO_4^=$ E and ASTM C1580 are similar to the Hach method except for these methods standards are prepared at 5 ppm intervals from 0 to 40 ppm, as barium sulfate suspensions above 40 ppm are unstable. SMEWW 4500-$SO_4^=$ E recommends checking the reliability of the curve by running a standard after every 3 or 4 samples. The AASHTO T290B method requires a standard curve prepared at concentrations of 0.0, 4.0, 10.0, 20.0, 30.0, 40.0, 60.0, 80.0, and 100.0 ppm; both AASHTO T290B and ASTM C1580 state that a separate calibration curve must be prepared for each photometer and if any change is made to the photometer or its cell, lamp, or filter, or to the reagent. The curve is checked with each series of sample tests by running two or more solutions of known sulfate concentrations. USEPA 9038 requires that a calibration curve with a minimum of one blank and three standards be prepared every hr; that the calibration curve be checked with an independently prepared standard every 15 samples, and that a duplicate spike sample be run every 10 samples.

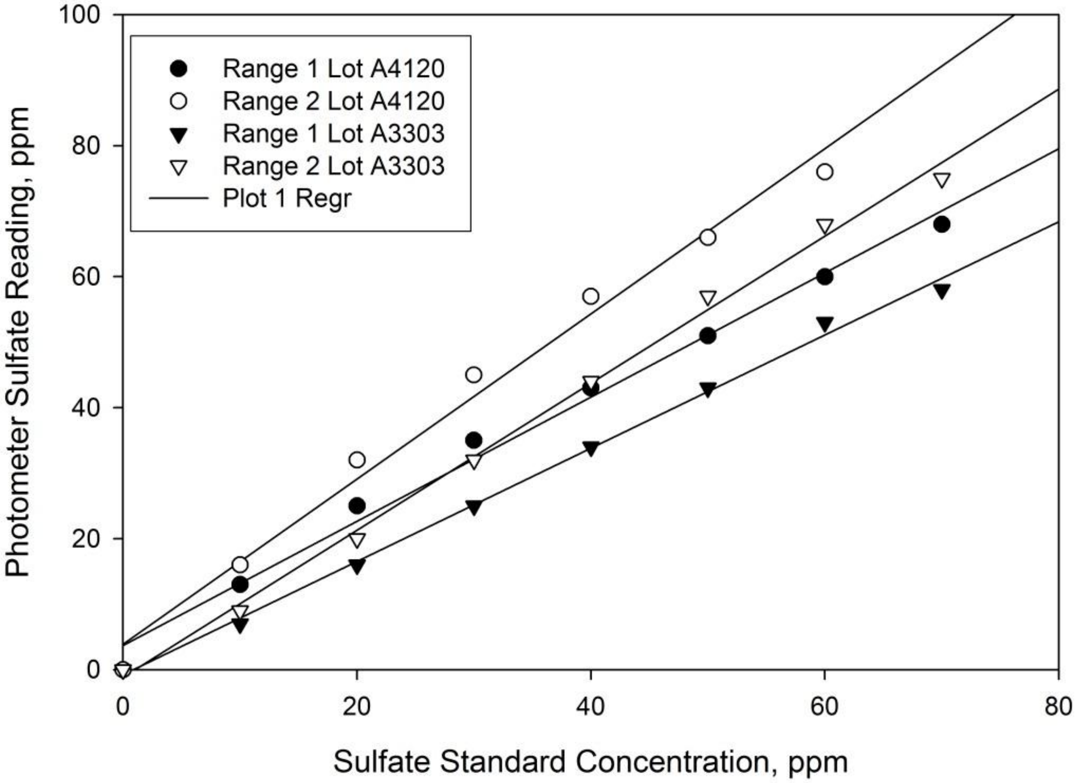


Figure 3-5. Hach Pocket Colorimeter II Analysis System for Sulfate pre-programmed sulfate calibration curves by range selection and reagent lot.

3.5.3.3 Soil testing

The Hach sulfate method uses pre-packaged barium chloride and citric acid, which are added directly to sample in the test cell; all other mentioned methods adjust the pH sample into the acid range and stir barium chloride crystals with an aliquot of sample and then decant the sample into a test cell for an absorption reading. AASHTO T290B is similar to SMEWW 4500-$SO_4^{=}$ E, with up to 50 mL of sample volume and a 4-cm instead of a 2-cm path length. Aliquots of a distilled water/glycerin solution and a sodium chloride/hydrochloric acid solution are added to the sample as a conditioner. Likewise, ASTM C1580 and USEPA 9038 are similar to SMEWW 4500-$SO_4^{=}$ E, except that in ASTM C1580 for each sample, four subsamples are prepared, each with different dilutions, with the expectation that these subsamples will bracket the sulfate concentration. Both ASTM C1580 and USEPA 9038 add to the sample a conditioner made of distilled water, hydrochloric acid, ethanol, sodium chloride, and glycerol.

3.5.4 Estimate of method precision and bias

For a multi-laboratory study the USEPA 9083 reported for a mixed ion water sample with 259 ppm sulfate a multi-laboratory %RSD and %RE of 9.1% and 1.2%, respectively. Multi-laboratory precision for ASTM C1580 was 21.2%; therefore, at the 95% confidence level, results of two properly-conducted tests in different laboratories on the same material were not expected to differ by more than 60%.

3.6 Summary

For AASHTO, ASTM, and USEPA methods that in many ways compare closely with the FMs for corrosion AQC, many differences exist in the procedural details. Differences that merit further attention include but are not limited to

For pH:

- *in-situ*, on-site, as-received, and air-dried pH;
- Transport temperature;
- Soil volume and water-to-soil ratio;
- Equilibration time and technique;
- Measurement temperature; and
- Use of 1 M potassium chloride or 0.01 M calcium chloride for dilution water.

For minimum resistivity:

- Soil drying, sieving, and water equilibration;
- Initial soil volume;
- Water quality;
- Meter calibration; and
- Soil versus water fraction of slurry in soil box.

For chloride:

- Drying time and temperature;
- Extraction time and method;
- Technique(s) to clarify sample;
- Use of check standards;
- Enhancement of the titration end point color change; and
- A check for significant interferences.

For sulfate:

- Drying time and temperature;
- Extraction time and method;
- Technique(s) to clarify sample;
- Calibration curve intervals and range;
- Use of check standards; and
- A check for significant interferences.

4 Trends in Select Backfill

Trends in backfill properties were investigated to (1) identify sources and source regions of acceptable MSE wall backfill with FDOT's Districts 1 and 7, and for these districts (2) review databased results of MSE wall backfill (material 092L) for failure trends in pH, minimum resistivity, chloride, and sulfate acceptance tests.

4.1 Spatial Trends

4.1.1 Methods

FDOT's District 1 and District 7 Materials Office maintains a local database to document by county the preliminary sampling conducted on potential MSE wall backfill sources in support of district construction projects. This database includes fields for the project identification number, project transfer and date if a source was sampled for one project and test results transferred to another project, stockpile or borrow pit number, survey date, test results for stratum sampled, the fraction of soil passing a number 200 sieve (200%), % organic matter (%OM), liquid limit (LL), plasticity index (PI), AASHTO soil group, plus the address and geo-coordinates of material source and remarks. The remarks field often contains the mine name and/or number, additional location information, and whether or not the material passed for embankment or MSE wall backfill. Multiple samples are typically obtained during preliminary sampling of a stockpile or borrow pit, and test results for 200% and %OM are input into the database as a range.

The districts' database was re-configured into a form that could be imported into Microsoft's Access database and queried with search terms such as district, county, project number, survey date, or mine name. For records with limited location information, the street address, road intersection or mine name were researched to get an approximate latitude and longitude for the source material. Not all records contained enough information to identify the source or source location; these records were removed from the Access database. The Access database was queried for separate listings by district of all sources tested and for those sources that were accepted for MSE wall backfill. In the latter case, the database query included passing test results for the upper limits of 200% and %OM, passing results for LL and PI, and excluded records for which the remarks indicated the material failed for MSE wall backfill. With ESRI's ArcMap 10.1 geographical information system (GIS) were plotted the location of each source along with a symbol proportional to the number of times the source appeared as a record in the database (Figures 4-1, 4-2, and 4-3). Also included in Figures 4-1 and 4-2 were the locations of commercial sand and gravel mines that produced more than 45,000 metric tons of material in 2001 within FDOT's District 1 and District 7 (USGS, 2002).

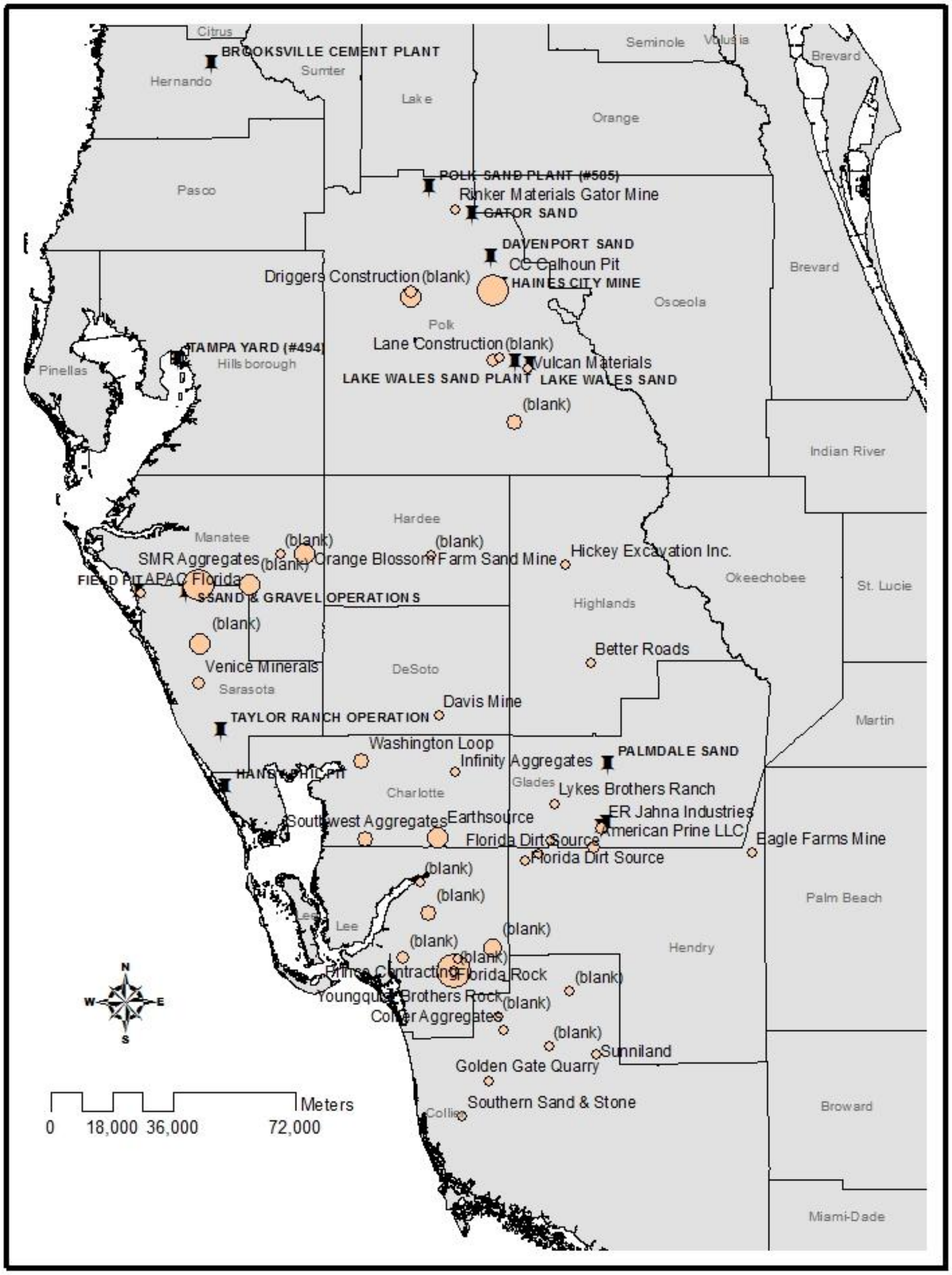


Figure 4-1. FDOT's District 1 sources tested for MSE wall backfill (circles: small = 1 record, large = 10 records) and construction sand and gravel mines that in 2002 produced more than 45,000 metric tons (pushpin).

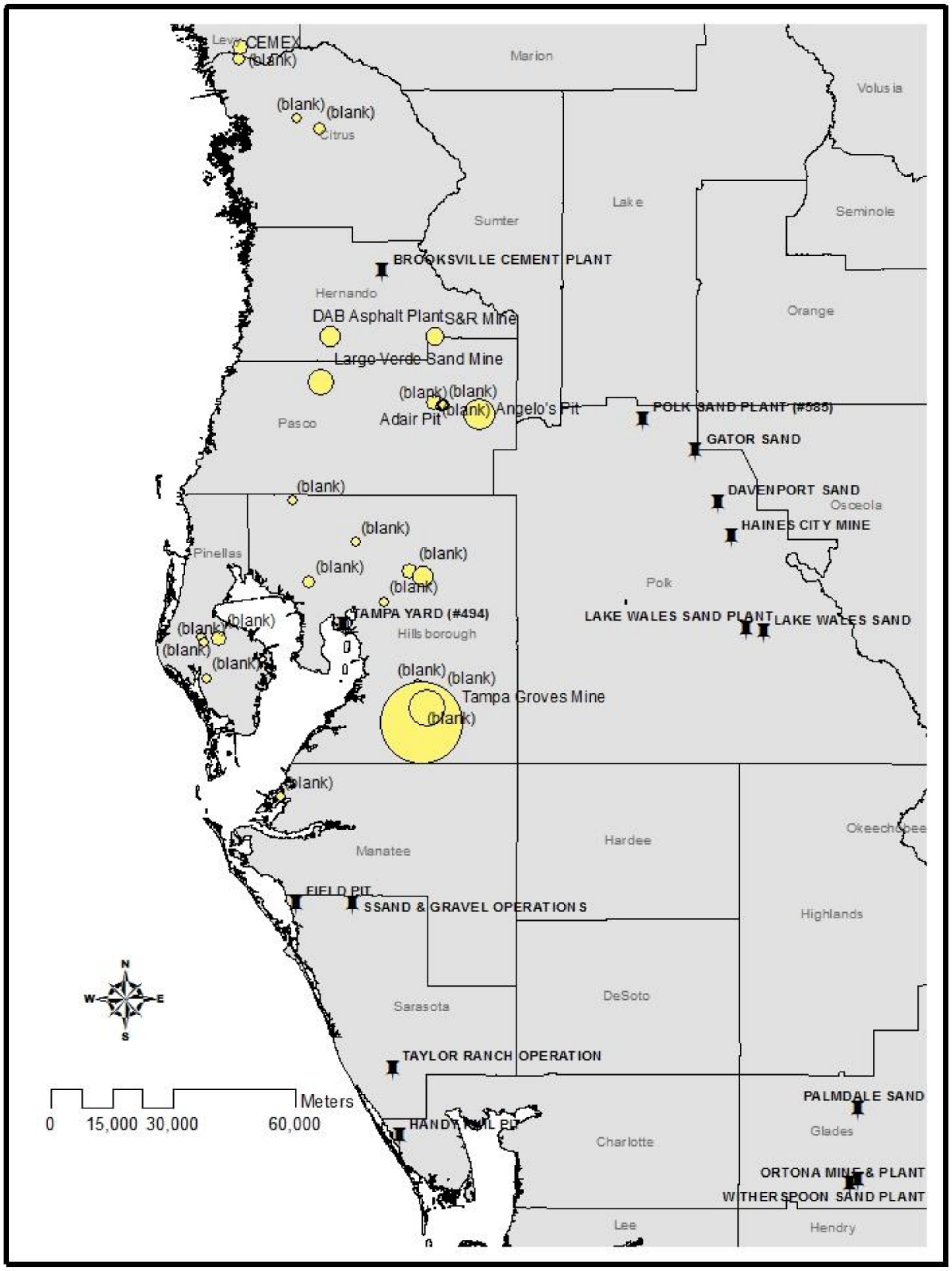


Figure 4-2. FDOT's District 7 sources tested for MSE wall backfill (circles: small = 1 record, large = 100 records) and construction sand and gravel mines that in 2002 produced more than 45,000 metric tons (pushpins).

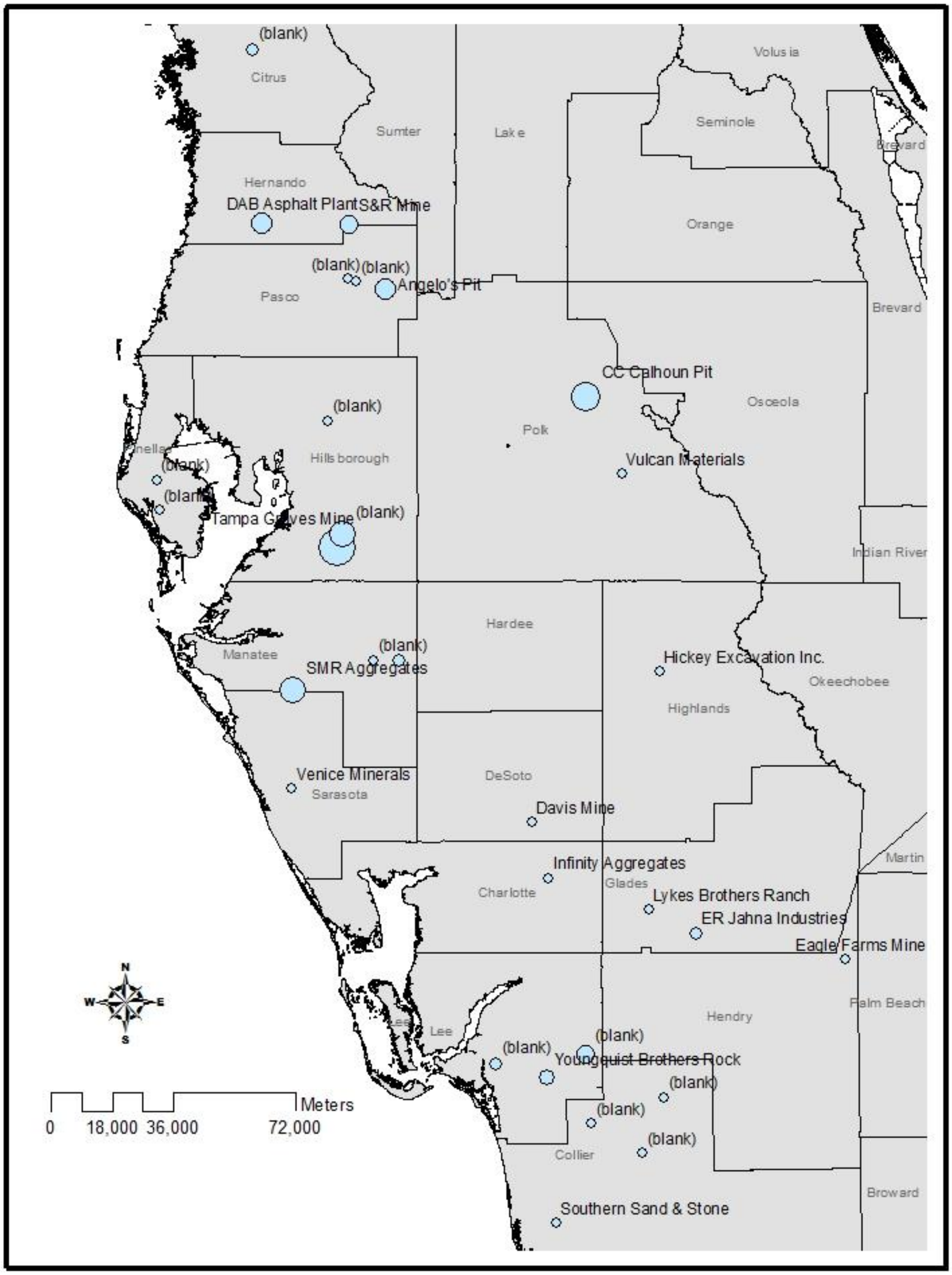


Figure 4-3. FDOT's District 1 and District 7 sources passed for MSE wall backfill (circles: small = 1 record, large = 10 records).

4.1.2 Results and discussion

Figure 4-1 and 4-2 show the dispersed locations of sources tested for MSE wall backfill within FDOT's District 1 and 7; more so for District 1 than for District 7. Only 30 of the 73 mapped sources had material that passed for MSE wall backfill (Figure 4-3); many of the sources were not commercial mines. Approximately 50% of the 43 sources that had material fail for MSE backfill, had material fail to meet gradation requirements (Chapter 2, Section 2.1.1, Table 2.1). Tampa Groves Mine (and neighboring mines) and CC Calhoun Pit were important backfill sources for Hillsborough and Pinellas Counties and for Polk County, respectively. MSE wall backfill sources were relatively scarce in some counties including the more metropolitan Hillsborough, Pinellas, and Polk Counties (Figure 4-3).

The links between the borrow pit or stockpile source, certification data, and corrosion AQC acceptance data as downloaded from Laboratory Information Management System (LIMS) were for the most part broken. Although the C-22 card does ask for plant or pit number, this information was largely missing from the LIMS records, possibly because material was obtained from on-site or because no plant or pit number was included in the material certification. A recommendation is that future documentation include the geo-coordinates (latitude and longitude, for example) of the borrow pit or stockpile of certified MSE wall backfill and that these geo-coordinates accompany the certification data as well as the acceptance data into LIMS.

4.2 Failure Trends

4.2.1 Methods

The LIMS database is an FDOT-resource for laboratory data input, storage, and retrieval, with features that assist with QA/QC and with data tracking, mining, and analysis. LIMS was accessed to retrieve FM test results and related project information. For this project, LIMS was entered via an "ad hoc" report, which could be modified to select or reject fields and to query for selected tables. The fields chosen for this analysis were District, County Code, Project ID, Test Code, Date Sample Taken, Sample ID, Sample Number, Lab ID, Assay Results, Sample Type, and Plant or Pit Number. The query was written to select only those records with Date Sample Taken after 2/20/2002; with Material ID (Specification Table) = 092L, which is the material for MSE wall backfill; and for Test Code (Test Table) = FM5-550 or FM5-550A or FM5-550B or FM5-551 or FM5-552 or FM5-553, which corresponded to pH, pH for MSE walls with metal strips, pH for MSE walls with polymer strips, minimum resistivity, chloride, and sulfate, respectively. In most cases, Sample ID and Sample Number corresponded with a suite of corrosion tests from a common test date. Lab ID referred to the independent or FDOT laboratory that tested the material. Sample types were Q, V, or R, for the contractor's quality assurance sample, the CEI's verification sample, and infrequently the resolution sample, respectively.

From LIMS, data were retrieved as a table with 16,283 records and copied into Microsoft's Excel® 2010 spreadsheet for further editing. The unedited table containing FDOT's District 1 and District 7 records were imported into the Access database. Only FDOT's District 1 and District 7 AQC acceptance test data were included in the analysis of statistical trends; these data were edited. FM5-550 A was renamed to FM5-550A, and the below records were removed:

- Duplicate records;
- Records with blank test results;
- Records with either an '<' or an '>' alongside a number; and
- Resistivity records before August 2010, as before this date units on the test result appeared to both ohm-cm and ohm-m, but after this date with two exceptions, units appeared to be ohm-m.

Four additional records were removed as outliers: one record with a sulfate concentration >5000 ppm and three records with a minimum resistivity less than 1 ohm-m.

StatSoft's Statistica 12 is a commercially-available statistical software application that features advanced query features, a visual analytic workspace, and reporting tables. Statistica 12 was employed to transform data, compile summary statistics, perform inference tests, generate frequency tables, and create normal probability graphs, as examples.

4.2.2 Results and discussion

Summary statistics revealed important information and potential trends about the underlying data (Table 4-1). For normally-distributed data, as an example, the mean, median, and mode are the same. These conditions were not met for any of the corrosion AQC test data, and a Kolmogorov-Smirnov (K-S) test for normality confirmed that the distributions were not normal ($p<0.05$).

Table 4-1 Statistics for FDOT's District 1 and 7 MSE Wall Backfill Corrosion Tests

Variable	Group	Valid N	Mean	Median	Mode	Frequency of Mode	Min	Max	10th Percentile	25th Percentile	75th Percentile	90th Percentile	St Dev
pH	All	536	6.9	7.0	8.2	19	4.0	9.9	5.3	6.1	7.9	8.4	1.1
	1	124	7.4	7.5	7.2	8	4.9	8.8	6.1	7.0	8.2	8.4	0.9
	7	412	6.8	6.8	7.3	14	4.0	9.9	5.2	5.9	7.8	8.2	1.1
Minimum Resistivity (ohm-m)	All	528	250	130	120	19	10	1,500	30	59	360	620	280
	1	82	120	90	Multi	4	15	380	40	56	170	260	88
	7	446	272	150	120	15	10	1,500	28	60	400	680	300
Chloride (ppm)	All	706	60	56	60	266	1.0	780	23	30	60	75	78
	1	106	38	30	30	39	1.0	90	15	30	60	60	19
	7	600	64	60	60	242	2.0	780	23	30	60	90	84
Sulfate (ppm)	All	673	61	39	0.0	67	0.0	1,080	0.5	12	81	141	78
	1	105	57	44	4.8	8	0.0	204	4.8	14	77	137	51
	7	568	62	38	0.0	65	0.0	1,080	0.0	11	81	143	82

The minimum, maximum, and percentile statistics revealed that one or more samples failed to meet the acceptance criteria. From Table 4-1, at least two backfill samples but not more than 10% of the samples in District 1 and 7 were below the acceptance limit of pH 5; likewise, at least one backfill sample but not more than 10% of the samples is District 7 were above the acceptance limit of pH 9. From the frequency tables generated in Statistica 12:

- For pH, 3% of the samples were below pH 5 or above pH 9; the failure rate was 1% for District 1 and 4% for District 7 (zero and three samples were below pH 4.5 for District 1 and District 7, respectively);
- For minimum resistivity, 10% of the data were below the acceptance limit of 3000 ohm-cm (30 ohm-m); the failure rate was 6% for District 1 but 11% for District 7;
- For chloride, 4% of the data were above the acceptance limit of 100 ppm, all of these from District 7; and
- For sulfate, 4% of the data were above the acceptance limit of 200 ppm; the failure rate was 1% for District 1 but 5% for District 7.

These results suggested that except for minimum resistivity, overall failure rates were relatively low, but MSE wall backfill used in District 7 projects had a higher failure rate than did backfill used in District 1 projects.

Hypotheses were tested that between District 1 and District 7 the means and variances within corrosion AQC tests were not different. To do so, a *t*-test and *F*-test, respectively, were applied on the log-transformed data distributions for minimum resistivity, chloride, and sulfate; pH is already log-transformed (Figure 4-4). The log-transformed mean or standard deviations were significantly different at the 95% confidence level ($p < 0.05$), results that suggested the properties of the MSE wall backfill between the districts were different.

For inference testing, ideally the sample data are independent, normally distributed, and have equal variances. If the data are not normally distributed or the data sets do not have equal variance, the *t*-test results are approximately correct when the data set is large (Ott, 1993). For inference testing, at least two other options are available: data transformation or a non-parametric inference test. A log transformation is often applied to data sets with a positive skew (Ott, 1993). Except for log-transformed minimum resistivity, log-transformed data distributions were not normally distributed but were a better match to a normal distribution than the un-transformed distribution (Figure 4-4); thus, for pH, chloride, and sulfate, the probabilities returned by the inference tests were only approximate.

Hypothesis 1: mean (District 1) = mean (District 7)
Hypothesis 2: variance (District 1) = variance (District 7)

- pH: *t*-test, $p \ll 0.05$; *F*-test, $p \ll 0.05$; reject both hypotheses
- log Resistivity: *t*-test, $p \ll 0.05$; *F*-test, $p \ll 0.05$; reject both hypotheses
- log chloride: *t*-test, $p \ll 0.05$; *F*-test, $p = 0.07$; reject hypothesis 1; accept hypothesis 2
- log sulfate: *t*-test, $p = 0.53$; *F*-test, $p \ll 0.05$; accept hypothesis 1; reject hypothesis 2

Although the differences could be due to MSE wall backfill properties between the two districts, they could also be due to differences in sampling and analysis techniques. Proximity of District 7 backfill sources to the Gulf of Mexico may explain the higher average and standard deviation chloride concentrations; another explanation, however, is that a difference exists in method procedures used by major laboratories in each district. For example, for the same Hach Chloride Low Range Test Kit Model 8-P, 5-400 ppm, one laboratory may use a sample size of 23 mL and a soil chloride resolution of 15 ppm and another laboratory may use a sample size of 10 mL and a soil chloride resolution of 60 ppm.

Hypotheses were also tested that between Q and V samples, the means and variances within corrosion tests were not different. Since across both districts the same laboratory can on one project test the contractor's Q samples and on another project the CEI's V samples, differences were not expected, yet significant differences were found.

Hypothesis 3: mean (Q) = mean (V)
Hypothesis 4: variance (Q) = variance (V)

- pH: *t*-test, $p = 0.10$; *F*-test, $p = 0.06$; accept both hypotheses
- log minimum resistivity: *t*-test, $p = 0.34$; *F*-test, $p \ll 0.05$; accept hypothesis 3, reject hypothesis 4

- log chloride: *t*-test, $p << 0.05$; *F*-test, $p << 0.05$; reject both hypotheses
- log sulfate: *t*-test, $p << 0.05$; *F*-test, $p = 0.18$; reject hypothesis 3, accept hypothesis 4

In most but not every case Q and V samples came from the same backfill, albeit sampled at a different time or from a different location within the MSE wall during the emplacement process. The exception to this case is for borrow pit or stockpile sampling as those samples were likely coded as V. Evidence for this is that of 2443 records of edited LIMS data, 1570 or 64% were coded V. Thus, one explanation for these test results is that there is some segregation between laboratories that perform Q and V tests; for example, FDOT's Districts 1 and 7 Materials Office may perform only V tests.

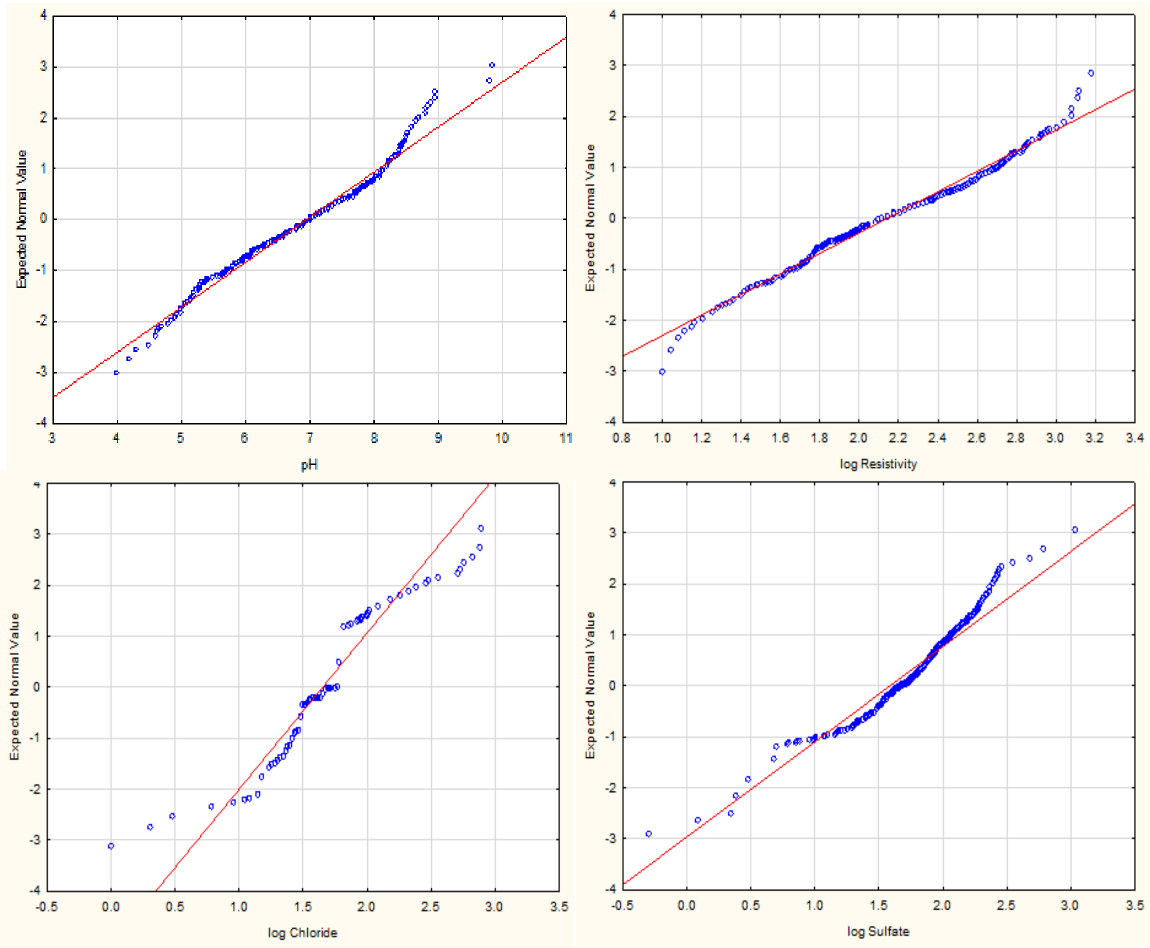


Figure 4-4. Normality plots for pH and log-transformed minimum resistivity, chloride, and sulfate.

4.3 Summary

In summary, of the 73 potential MSE wall backfill sources databased by FDOT's Districts 1 and 7 Materials Office laboratory, backfill from only 30 sources passed the geotechnical and corrosion requirements. Approximately 50% of the 43 sources that were screened for MSE backfill had material fail to meet gradation requirements. MSE wall backfill sources were widely dispersed across Districts 1 and 7, and were relatively scarce in some counties including in the more metropolitan Pinellas, Hillsborough and Polk Counties.

The frequency of failure rates for corrosion properties of MSE wall backfill based on the LIMS data set suggested that except for minimum resistivity with a 10% overall failure rate, failure rates were relatively low. MSE wall backfill used in District 7 projects had a higher failure rate than backfill used in District 1 projects.

MSE wall backfill corrosion properties varied significantly between District 1 and 7, results that could be explained by differences in the backfill or by differences in sampling and analysis techniques by the major laboratories in each district. The quality control or Q samples and the verification or V samples varied significantly for some but not all corrosion properties, which suggested that some segregation was present between laboratories that performed Q versus V samples.

The links between the borrow pit or stockpile source, certification data, and corrosion AQC acceptance data as downloaded from LIMS were for the most part broken. A recommendation is that future documentation include the geo-coordinates (latitude and longitude, for example) of the borrow pit or stockpile of certified MSE wall backfill, and that these geo-coordinates accompany the certification data as well as the acceptance data into LIMS.

5 Single-Laboratory Precision and Bias

5.1 Definitions of Precision, Accuracy, and Minimum Detection Level

5.1.1 Approaches to calculating accuracy and precision

A measured value y is the sum of its unknown true value μ plus an unknown measurement error ε (Montgomery, 2005) (Equation 5-1), where ε consists of both a fixed component (bias) and a random component.

$$y = \mu + \varepsilon \tag{5-1}$$

In many situations, unknown μ may be represented as known, for example, when μ is a certified, traceable, or consensus value or when μ was determined by a method with ε that is low in comparison to the method that produced y (Rice et al., 2012). If the random component of ε is negligible, the fixed component or bias of ε can be estimated from Equation 5-2.

$$\varepsilon = y - \mu = \varepsilon_{random} + \varepsilon_{bias} \tag{5-2}$$

A generalized expression of relative error %RE is presented in Equation 5-3 for the case where μ is treated as known and y_i is the i^{th} observation of y. The sign is retained to indicate the direction of bias. The lower is the %RE the more accurate is the method.

$$\%RE = 100 \cdot \frac{1}{n}\sum_{i=1}^{n} \frac{(y_i - \mu)}{\mu} \tag{5-3}$$

For the case of unknown μ, however, Equation 5-4 is more appropriate.

$$\%RE = 100 \cdot \frac{(y_{max} - y_{min})}{\frac{1}{n}\sum_{i=1}^{n} y_i} = 100 \cdot \frac{(y_{max} - y_{min})}{\bar{y}} \tag{5-4}$$

Another and related measure of accuracy is the amount of analyte added to a sample that is recovered by the method. Recovery is calculated using Equation 5-5, where C_{s+ms} is the analyte concentration in the sample with a matrix spike, C_s is the analyte concentration in the sample without a matrix spike, and C_{ms} is target concentration of the matrix spike.

$$\%Recovery = 100 \cdot \frac{C_{(s+ms)} - C_s}{C_{ms}} \tag{5-5}$$

The usual measure of data scatter is standard deviation σ and estimates of σ are represented at s, where s has both a random and a systematic component. Youden (1975) explained that the random component is determined from replicate measurements in the same laboratory under the same conditions, while the systematic component is introduced under differing conditions in the same laboratory, for example, another operator, or between laboratories. Youden (1975) noted that if other laboratories were not following the same procedures for reasons such as ambiguous instructions or undefined environmental factors, then random error would vary between laboratories as well. In general, however, the terms random and systematic are often used interchangeably with single-operator and multi-laboratory, respectively, in reference to components of variance.

Similar to Youden (1975), Rice et al. (2012) referred to the random component of method standard deviation as the repeatability of a method s_r, which is estimated by pooling sample standard deviations s_{ri} of measurements of N different specimens as shown in Equation 5-6 (Rice et al., 2012). A standard deviation that characterizes both random and systematic errors is the reproducibility of a method s_R. A method with lower s_r or s_R is a more precise method.

$$s_r = \sqrt{\frac{1}{N}\sum_{i=1}^{N} s_{ri}^2} \qquad (5\text{-}6)$$

Another and related measure of precision is the relative standard deviation %RSD, as defined in Equation 5-7, and applies generally to either σ or s; that is, to either population or sample statistics (Skoog et al., 1996); %RSD is synonymous with coefficient of variation (CV).

$$\%RSD = 100 \cdot \frac{s}{\bar{y}} = CV \qquad (5\text{-}7)$$

5.1.2 Method limit of detection (LOD) and limit of quantitation (LOQ)

5.1.2.1 Definition of LOD and MDL

The limit of detection (LOD) is defined by Ellison et al. (2009) as the “minimum concentration of the analyte that can reliably be detected with a specified level of confidence.” The general features of an LOD experiment or a similar method detection level (MDL) experiment are (Ellison et al., 2009; Rice et al., 2012):

- 7 to 20 replicate samples containing either no analyte (blank samples) or a low-level of analyte are analyzed over a period of days;
- For analysis of a low-level of analyte, the analyte concentration should be in the range of 1 to 5 times the LOD; and
- For a method LOD (or method detection level MDL), replicate samples must be processed through the entire method.

LOD is calculated according to Equation 5-8 using the average blank concentration x_0 and standard deviation s, and the one-tailed Student’s t value for the experimental degrees of freedom ν and at the specified error levels, for example, 5% for both Type I (α) and Type II (β) errors (Ellison et al., 2009). The values for x_0 and k_1 are 0 and 1, respectively, if observations have independent baseline corrections; x_{blank} and 1, respectively, with no baseline correction, and 0 and $k_1 = \sqrt{1 + \frac{1}{N_{bl}}}$, respectively, where N_{bl} are the number of observations averaged to obtain the baseline correction, for observations without independent baseline corrections (Ellison et al., 2009). For $x_0 = 0$, $k_1 = 1$, $\alpha = \beta = 0.05$, and number of samples $N = 7$, Equation 5-8 simplifies to Equation 5-9.

$$LOD = x_0 + k_l s t_{(\nu,\alpha)} + k_l s t_{(\nu,\beta)} \tag{5-8}$$

$$LOD = 3.88 \cdot s \tag{5-9}$$

For comparison, MDL is calculated according to Equation 5-10, where the specified level of a Type I error is 99% and for $N = 7$ simplifies to Equation 5-11 (Rice et al., 2012; FDEP, 2009).

$$MDL = s t_{(\nu,\alpha)} \tag{5-10}$$

$$MDL = 3.14 \cdot s \tag{5-11}$$

5.1.2.2 Definition of LOQ

The limit of quantitation (LOQ), or similarly the practical quantitation limit (PQL), is defined as the “lowest concentration of analyte that can be determined with an acceptable level of uncertainty” (Ellison et al., 2009) and takes into account variations in LOD or MDL from laboratory to laboratory. Ellison et al. (2009) describes LOQ as 10 · s; Rice et al. (2012) as ~5 · MDL.

5.1.2.3 Calculation of Standard Deviation

The standard deviation associated with the baseline-corrected analyte concentration is given in Equation 5-12, where s_s is the sample standard deviation and s_{bl} is the blank standard deviation.

$$s = \sqrt{s_s^2 + s_{bl}^2} \tag{5-12}$$

If $s_s = s_{bl}$, then Equation 5-12 is simplified to $s = \sqrt{2}\, s_s$.

5.2 Single Laboratory, Aqueous Standards

5.2.1 2011 version of FMs for pH, minimum resistivity, chloride, and sulfate

Aqueous standards traceable to the National Institute for Standards and Technology (NIST) for pH, conductivity, chloride, and sulfate were obtained from reputable sources and tested in USF’s soil laboratory. For pH, standards were buffer solutions of pH 5.00 ± 0.01 (25°C) and pH 9.00 ± 0.01 (25 ^{o}C); for minimum resistivity, the standard was a sodium chloride conductivity solution prepared at 250 ± 1 µS/cm (25°C) or 4000 ± 16 ohm-cm (25°C); for chloride, the standard was a sodium chloride solution prepared at 100.0 ± 0.3 ppm as chloride; and for sulfate, the standard was a potassium sulfate solution prepared at 202.0 ± 0.2 ppm as sulfate. Resistivity and pH standard concentrations corrected to an ambient temperature of 21 ^{o}C were resistivity 4,167 ± 17 ohm-cm, pH 4.98 ± 0.05, and pH 9.02 ± 0.05. The pH and conductivity standards were tested without dilution; however, the chloride and sulfate standards were diluted by a factor of three, and the diluted solutions decanted through a coarse filter as is done in the extraction process. The sulfate standard required further dilution by a factor of two. Results were summarized in Table 5-1. A one-sided *z*-test was applied to test the hypothesis that the standard concentration was higher than the observed concentration. The *z*-test was significant for chloride and sulfate concentrations with biases of 5 ppm and 10 ppm, respectively.

Table 5-1 Accuracy and Precision of FM for pH, Minimum Resistivity, Chloride, and Sulfate Based on Aqueous Standards (2011 Version of FMs)

FM	N	Average	St Dev, s_r	%RSD	%RE
pH	5	5.00	0.01	0.23	0.32
pH	5	9.02	0.00	0.00	-0.22
Resistivity, ohm-cm	5	4,160	198	4.76	-0.17
Chloride, ppm	5	95.1	5.34	5.62	-4.90
Sulfate, ppm	3	192	6.00	3.13	-4.95

In USF's soil laboratory, pH measurements with NIST-traceable buffers at pH 5.00 and pH 9.00 were made with no significant bias and with precision comparable to those reported for the buffers. Likewise, resistivity of a 4,000 ohm-cm solution was made with no significant bias and with a %RSD within the 5% mid-scale precision reported by the equipment manufacturer. Measurements of both chloride and sulfate, however, had biases of -5%, which were significant. For chloride, such a bias could have been caused by error in the blank determination; for sulfate the bias could have been caused by error in the calibration curve. For both, error in volumetric measurements could have been a source of bias. The single laboratory or repeatability s_r and %RSD were somewhat high because of the sample dilution. For example, a sample of 200 ppm sulfate must be diluted by a factor of ~6 to obtain a consistent photometer reading, thus a change of one ppm on the photometer reading equates to a change of six ppm in the sample.

5.2.2 Proposed revised FMs for pH, minimum resistivity, chloride, and sulfate

Aqueous standards traceable to the NIST for pH, conductivity, chloride, and sulfate were obtained from reputable sources and tested in USF's soil laboratory and results were summarized in Table 5-2. Refer to Table 5-2 for pH and resistivity of temperature-corrected standard concentrations. For pH, the Accumet meter/electrode AB150/13-620-631 was calibrated with three standard buffers, nominally pH 4, 7, and 10. Test buffers included two purchased normal-ionic strength buffers (pH 5.00 and pH 9.00 at 25°C), two purchased low-ionic strength buffers (pH 4.10 and pH 6.97 at 25°C), and two very low-ionic strength buffers (pH 4.00 and pH 5.00) prepared in the USF soils laboratory from NIST-traceable 0.02 N hydrochloric acid. For pH, the test temperature was 20°C and all measurements were made on the same day. Minimum resistivity was tested using a Nilsson Model 400 analog meter and a McMiller 280-mL soil box with both a 250-µS/cm (4,000 ohm-cm) and a 500-µS/cm (2,000 ohm-cm) sodium chloride conductivity standard. Three measurements were made with each standard one day apart, with measurement temperatures of 23°C and 21°C on the first and second day, respectively. Chloride and sulfate were tested using their respective Hach kits with 100 ppm standards diluted by a factor of three to be within the range of the test kits. For chloride and sulfate, three measurements were made with each standard two days apart, and different lot numbers for the Chloride 2 indicator (potassium dichromate and sodium bicarbonate) and SulfaVer 4 reagent (barium chloride and citric acid) were used on consecutive days.

Table 5-2 Accuracy and Precision of FM for pH, Minimum Resistivity, Chloride, and Sulfate Based on Aqueous Standards (Proposed Revised FMs)

FM	Standard	N	Avg	St Dev	%RSD	%RE
pH	ϒ4.01	3	4.00	0.012	0.29	-0.33
pH	*4.10	3	4.07	0.010	0.24	-0.73
pH	4.98	3	5.03	0.010	0.20	1.00
pH	ϒ5.00	3	4.99	0.012	0.23	-0.27
pH	*6.98	3	6.88	0.006	0.08	-1.38
pH	9.05	3	9.00	0.006	0.06	-0.52
Min Res, ohm-cm	4,170	3	4,200	0	0.00	0.72
Min Res, ohm-cm	2083	3	2,050	50	2.40	-1.58
Min Res, ohm-cm	4,350	3	4,383	58	1.33	0.77
Min Res, ohm-cm	2,174	3	2,150	50	2.30	-1.10
Chloride, ppm	100	6	97.5	8.22	8.22	-2.50
Sulfate, ppm	100	6	99.5	10.6	10.6	-0.50

ϒLow-ionic strength buffers prepared from 0.02 N HCl; *Commercially-available low-ionic strength buffers

Overall the results were not too different for the proposed revised FMs than for the 2011 versions. For the proposed revised FMs, pH precisions were within those given for the standards; the only significant (*z*-test, $p = 0.04$) bias was seen for the regular-ionic strength pH 5.00 buffer (1 %RE). Minimum resistivity precisions trended lower and biases higher, but for chloride and sulfate these trends were reversed. Bias statements were developed for each proposed revised FM from the results shown in Table 5-2.

5.2.2.1 Bias statement FM for pH

Single-operator, single laboratory bias for this method using an Accumet meter/electrode AB150/13-620-631 was evaluated at 20°C with repeated measures of each six aqueous standards ranging from pH 5.00 to pH 9.00. The average bias was -0.01 pH units.

5.2.2.2 Bias statement FM for minimum resistivity

Single-operator, single laboratory bias for this method was evaluated using a Nilsson Model 400 analog meter and a McMiller 280-mL soil box and repeated measures of two aqueous standards with resistivities at 25°C of 2,000 ohm-cm and 4,000 ohm-cm. After correcting for measurement temperatures in the range of 21°C to 23°C, average biases were -30 ohm-cm (-1.3%) for the 2,000 ohm-cm standard and 30 ohm-cm (0.7%) for the 4,000 ohm-cm standard. With no correction for temperature, average biases were 100 ohm-cm (5%) for the 2,000 ohm-cm standard and 300 ohm-cm (7%) for the 4,000 ohm-cm standard.

5.2.2.3 Bias statement FM for chloride

Single-operator, single laboratory bias for this method was evaluated using a Hach Chloride Low Range Test Kit Model 8-P, 5-400 ppm, and repeated measures of a 100-ppm aqueous standard, which was diluted by a factor of three to be in the target range of the test kit. Six replicate standards were tested, three with one lot number and three with a different lot number of Chloride 2 indicator. The average bias was -2.5 ppm (-2.5%).

5.2.2.4 Bias statement FM for sulfate

Single-operator, single laboratory bias for this method was evaluated using a Hach Sulfate, Pocket Colorimeter II Test Kit and repeated measures of a 100-ppm aqueous standard, which was diluted by a factor of three to be in the target range of the test kit. Six replicate standards were tested, three with one lot number and three with a different lot number of SulfaVer 4 reagent. The average bias was -0.5 ppm (-0.5%).

5.3 Single Laboratory, Proficiency Test Soil

Santa Fe River soil (Chapter 7, Section 7.3, Table 7-1) was air-dried and sieved through a No. 10 (2 mm) mesh and replicate samples were prepared according to AASHTO T248. With this soil, repetitive measurements were made according to the FMs for pH, minimum resistivity, chloride, and sulfate in USF's soil laboratory. Chloride and sulfate concentrations were low in the Santa Fe River soil, at or below the LOD or MDL. Thus, chloride and sulfate were added to this soil in the form of solid sodium chloride or sodium sulfate such that the minimum resistivity was near 3,000 ohm-cm. Typical amendments were 0.1 g/kg of sodium chloride and 0.1 g/kg of sodium sulfate with and without 0.01 g/kg sodium bisulfate, or 0.25 g/kg sodium sulfate. Salts were added to the soil and then mechanically mixed for 10 min in 3-kg batches. As necessary, multiple batches were mixed and mechanically split per AASHTO T248 to obtain about 1,200 g per replicate, which was sufficient soil for all four corrosion tests. Amendment with sodium bisulfate was tried as a way to lower pH but at 0.2 g/kg sodium bisulfate the soil resistivity reached ~3,000 ohm-cm with little change in pH. Dilution water was deionized water from USF's Nanotechnology Research and Education Center, which typically had a resistivity greater 1,000,000 ohm-cm. Nine replicates of Santa Fe River soil were tested with and without salt-amendment; average, standard deviation, %RSD and %RE were reported in Table 5-3.

Table 5-3 Accuracy and Precision of Florida Methods for pH, Minimum Resistivity, Chloride, and Sulfate with Santa Fe River Soil

FM	N	Average	St Dev, s_r	%RSD	%RE
pH					
No amendment	9	7.97	0.06	0.73	2.13
Salt amendment*	9	7.95	0.07	0.88	2.39
Minimum Resistivity, ohm-cm					
No amendment	9	15,900	782	4.92	12.6
Salt amendment*	9	2,828	227	8.01	28.3
Chloride, ppm					
No amendment	9	-1	2	-193	837
Salt amendment*	9	65	12	18.9	61.0
Sulfate, ppm					
No amendment	9	37	27	71.4	240
Salt amendment*	9	99	8	8.19	90.9

* 0.1 g/kg sodium chloride, 0.1 g/kg sodium sulfate, and 0.01 g/kg sodium bisulfate

For pH measurement, %RE and %RSD were reasonably low, with or without sodium salts added. For minimum resistivity, %RE and %RSD increased when conducting salts were added, which may reflect a greater degree of heterogeneity between replicates rather than method factors. Note that for the unmodified soil, the %RSD was within the 5% mid-scale precision reported by the equipment manufacturer. For chloride, with no salts added the %RE and %RSD were very high, a strong indication that the chloride concentration in the sample was below the detection level. (A negative concentration for the average is possible with a blank subtraction, when the blank concentration is higher than the sample concentration). With salts added, the %RE and %RSD were still rather high, a result that suggested there was room for improvement in the method. The salt amendment increased the soil chloride concentration by 60 ppm compared with an observed average concentration of 65 ppm; this represented a chloride recovery of 107% and suggested that the average concentration of chloride in the unmodified soil may have been on the order of 5 ppm. For sulfate, with no salts added %RE and %RSD were high, an indication that the sulfate concentration in the sample was below the detection level. With salts added, %RE and %RSD were still rather high, a result that suggested there was room for improvement in the method. The salt amendment increased the soil sulfate concentration by 75 ppm compared with an observed average concentration of 99 ppm; this represents a sulfate recovery of 130% and suggested that the average concentration of sulfate in unmodified soil may have been on the order of 25 ppm.

Both LOD and MDL are common approaches to identify the level at which a signal emerges from noise. For a probability of Type I and Type II error of 5% and $N = 9$, the LOD for pH, minimum resistivity, and sulfate was $3.72 \cdot s$, with no baseline or independent baseline corrections, and $5.26 \cdot s$ for chloride, with one blank concentration measurement for several sample measurements. The MDL was $2.896 \cdot s$, given a Type I error of 1% and $N = 9$. LODs and MDLs were reported in Table 5-4.

Table 5-4 Level of Detection (LOD) and Method Detection Level (MDL) of Florida Methods for pH, Minimum Resistivity, Chloride, and Sulfate for Santa Fe River Soil

FM	N	LOD	MDL
pH			
No amendment	9	0.22	0.17
Salt amendment*	9	0.26	0.20
Minimum Resistivity, ohm-cm			
No amendment	9	2,910	2,260
Salt amendment*	9	842	656
Chloride, ppm			
No amendment	9	8	5
Salt amendment*	9	65	36
Sulfate, ppm			
No amendment	9	99	77
Salt amendment*	9	30	24

*0.1 g/kg sodium chloride, 0.1 g/kg sodium sulfate, and 0.01 g/kg sodium bisulfate

The LOD or MDL for pH and for minimum resistivity in salt-amended soil were far enough away from acceptance limits of pH 5.00 and 3,000 ohm-cm, respectively, and posed no problem for the current method. Likewise the LOD or MDL for sulfate, while high at 30 ppm or 25 ppm, respectively, was relatively distant from the acceptance limit of 200 ppm and therefore did not pose a problem for the current method. For chloride, however, the LOD approached 2/3 of the acceptance limit of 100 ppm, thus the LOD would benefit from method improvement.

5.4 Multiple Laboratories, Proficiency Test Soil

Starvation Hill soil (Chapter 7, Section 7.3, Table 7-1) was air-dried, sieved through a No. 10 (2 mm) mesh, and quartered according to AASHTO T248 into ~3 kg replicate samples. These samples were distributed to four laboratories, including USF's soil laboratory, and tested according to the FMs for pH, minimum resistivity, chloride, and sulfate analysis. Results were summarized in Table 5-5.

Table 5-5 Multiple Laboratory Results of Florida Methods for pH, Minimum Resistivity, Chloride, and Sulfate for Starvation Hill Soil

Laboratory	pH	Minimum Resistivity, ohm-cm	Chloride, ppm	Sulfate, ppm
1	6.60	4,100	26	24
2	7.75	23,810	8	3
3	5.60	5,300	60	3
4	7.57	23,500	3	14

For pH, multi-laboratory results reflected the range of pH measurement technique, instrumentation, and electrode condition seen in laboratory visits (Chapter 6). For minimum resistivity, the large disparities in readings pointed to differences in how the soil slurry was handled during testing: minimum resistivity would be lower if the water portion of the slurry was decanted into the soil box first and then topped with the soil portion of the slurry versus filling the box with mostly the soil slurry. Refer to Chapter 9, Section 9.2.7, for further discussion. For chloride and sulfate, results were consistent with levels near or below detection (Table 5-4).

5.5 Summary

Estimates of single laboratory precision (%RSD) and bias (%RE) were obtained with aqueous standards and with a proficiency test soil with FMs for pH, minimum resistivity, chloride, and sulfate. Across all four FMs, estimates of %RSD and %RE were higher for a soil sample than for aqueous standards as expected, but much higher for chloride and sulfate concentrations especially for chloride and sulfate concentrations below ~5 ppm and ~25 ppm, respectively. A preliminary multi-laboratory study with a proficiency test soil yielded disparate results for both pH and minimum resistivity, which suggested that significant differences in procedures or equipment existed between laboratories and merited further investigation.

6 Laboratory Visits

6.1 Introduction

Multi-laboratory contributions to method reproducibility were estimated pre- and post-method revision to assess improvement in pH, minimum resistivity, chloride and sulfate measurements. Prior to method development, on-site testing of a select backfill was conducted at six FDOT and nine commercial laboratories, with representative laboratories in each FDOT district.

6.2 Protocol

Dr. Noreen Poor conducted the visits. The protocol was similar between laboratories. Method operators were asked a standard set of questions regarding sample processing, soil extraction, and each of the FMs. Tests were done in the same order: minimum resistivity, pH, chloride, and sulfate. For resistivity and pH, operators were asked to test Santa Fe River soil that had been air-dried, sieved, and mechanically-split into 1,500-g subsamples. For chloride and sulfate, operators were asked to test 30 ppm chloride and 30 ppm sulfate standard solutions, respectively. These solutions were prepared in advance through dilution of NIST-traceable 1000-ppm stock solutions. Operators were also asked to do a few additional quality assurance/quality control (QA/QC) measurements along with the FMs. For resistivity, these included measurement of resistivity for (1) a 3,300-ohm resistor, (2) a 3,333 ohm-cm sodium chloride conductivity standard, and (3) the laboratory's dilution water. An audit measurement was also made with USF's resistivity meter of the soil box plus soil at the minimum resistivity. For pH, slope and offset were checked for working electrodes; and after completion of the operator's measurement, an audit measurement was made with USF's pH meter and electrode. For chloride, the use of a blank to check and adjust for chloride content in the dilution water was demonstrated. Finally, for sulfate, for those laboratories that were not using an instrument with a built-in conversion of light attenuation to sulfate concentration, a machine-specific calibration curve was prepared.

6.3 Laboratory Environment

For the participating laboratories, laboratory environments were somewhat different between commercial laboratories and FDOT laboratories. For commercial laboratories, MSE wall backfill samples were processed either as quality control or as verification tests. Facilities were those of a geotechnical rather than a chemistry laboratory: space was likely as not to be controlled for climate, noise, dust, or vapor; MSE wall backfill samples typically arrived in sufficient quantity for all required geotechnical and corrosion tests, and dilution water was typically purchased. Commercial laboratories processed anywhere from 1 to 30 samples per week, and estimated that on the average it took about two hr of labor to do all four corrosion tests. Although not required by FDOT, oversight for the corrosion methods came either from CMEC or AASHTO Materials Reference Laboratory (AMRL).

For FDOT laboratories, MSE wall backfill samples were typically processed as resolution tests. Facilities were more a combination of geotechnical and chemistry laboratories and likely to have ventilated and climate-controlled space, a fume hood, and on-site production of dilution water. MSE wall backfill samples typically arrived in sufficient quantity for all required geotechnical and corrosion tests or in a smaller quantity sufficient for all four corrosion tests. FDOT laboratories processed anywhere from 0 to 15 samples per week and estimated that on the average it took about three hr of labor to do all four corrosion tests. FDOT laboratories reported no oversight of the four corrosion methods, with the exception of FDOT's SMO Environmental Laboratory, which is accredited by the National Environmental Laboratory Accreditation Program (NELAP). FDOT's SMO Environmental Laboratory routinely tests chloride and sulfate levels in both water and soil samples.

Both FDOT and commercial laboratories tested core samples of soil and sediment, which at times did not contain enough soil for all four corrosion tests. In this case soil was typically removed for pH, chloride, and sulfate analyses and the remaining soil used for a resistivity measurement, where the volume of the soil box (270 mL or 80 mL) limited the minimum sample size. Water was added in 10% increments, for example, 50 mL increments for 500 g of soil or 25 mL for 250 g of soil.

6.4 Results

6.4.1 FM for pH

In general, pH measurements were inconsistent across all 15 laboratories. With one exception, no two pH meter/electrode systems were matched. Accumet, which is a pH meter marketed by Thermo Fisher Scientific and Cole Palmer, was the most common brand. The capabilities of pH meter/electrode systems also varied to include one or more combinations of pH, millivolts (mV), temperature (°C), conductivity, and ion specific electrode (ISE); most were bench top systems and all but one pH meter/electrode system had a glass electrode. Electrodes ranged in age from new to 10 years old; electrodes at three laboratories did not function properly and electrodes at four laboratories were suspect (high offset voltages, erratic readings, sensitivity to vibration, slow response time). Calibration of pH measurements ranged from a single pH 7 buffer calibration to a three-point calibration with pH 4, 7, and 10 buffers. Summary statistics from the laboratory visits (Table 6-1) were compared with those generated in the USF laboratory (Chapter 5, Section 5.3, Table 5-2), and audit measurements in each laboratory. Although the data sets summarized in Table 6-1 were based on Santa Fe River soil collected from FDOT's State Materials Office (SMO), soil sampling dates were November 11, 2013 for the USF laboratory results and March 10, 2014 for the inter-laboratory results.

Table 6-1 Summary Statistics for pH Measurements for a Sub-Sample of Air-Dried, Sieved, and Mechanically-Split Santa Fe River Soil

FM for pH	*N*	Average	St Dev (*s*)	%RSD	%RE
USF Laboratory	9	7.97	0.06	0.73	2.13
USF On-Site Audit	14	8.15	0.15	1.83	6.62
Laboratory Visits	15	7.85	0.80	10.1	32.4

For pH, the average, standard deviation *s*, %RSD, and %RE were higher for the USF on-site audit than for USF laboratory measurements and measurements between laboratories had a lower average but a higher standard deviation, %RSD, and %RE than for USF laboratory and on-site audit results (Table 6-1). Bias and thus accuracy remain undefined for a method in the absence of an accepted reference value, but a large %RE suggested the presence of systematic error. Refer to Table 6-2 for sources of variability in the FM for pH measurement between laboratories.

Following the guidance of ASTM E177, example method statements of precision generated from the between-laboratory statistics were:

> Soil pH measurements were made by 15 laboratories with randomly selected subsamples of an air-dried and sieved sandy soil. For a like material, approximately 95% of individual test results from laboratories similar to those in the inter-laboratory study can be expected to differ in absolute value from their average by less than 2.0 x *s* = 1.6 pH units.
>
> Soil pH measurements were made by 15 laboratories with randomly selected subsamples of an air-dried and sieved sandy soil. The average test value was 7.85 pH units, and the reproducibility limit (between laboratory) was 2.8 x *s* = 2.2 pH units.

In practical terms, if the pH average and standard deviation (laboratory visit *s* from Table 6-1) of the quality control and verification samples were 5.0 ± 0.8 pH units, the null hypothesis (H_0) that the soil pH was equal to pH 4 could not be rejected at the 95% confidence level. Likewise, if the pH average and standard deviation (laboratory visit *s* from Table 6-1) of the quality control sample and verification samples were 9.0 ± 0.8 pH units, the null hypothesis (H_0) that the soil pH was equal to pH 10 could not be rejected at the 95% confidence level. These results suggested that for pH, the multi-laboratory precision was not adequate. Note that *s* for pH was underestimated, as statistics generated by this study were limited to one soil and did not include variability from soil heterogeneity or from field sampling, transport, and storage of soil.

Table 6-2 Sources of Variability in pH between Laboratories

Transported soil at ambient vs cool temperatures
Stored soil under ambient conditions or in the refrigerator
Used 100 g or 100 mL of soil
Tested “as is” or air dried
Used soil from resistivity measurement
Waited zero to 30 min or more to test sample
Stirred once or up to three times
Put soil/water mixture on shaker table for three 10-min intervals
Stirred or did not stir sample during pH measurement
Measured pH as soon as stable light came on or waited until reading was stable for 1 min
Prepared soil water/mixture in a beaker, bottle, or disposable cup
Calibrated with one, two, or three buffers
Used fresh buffers or re-used buffers for calibration
Stored pH electrode in distilled water, tap water, buffer, KCl, or dry
Used glass electrode or solid state electrode
Refilled glass electrode or used disposable electrode
Kept electrode for up to 10 yr

In summary, for an average of two samples the multi-laboratory precision was not adequate to assure that a pH 5 or pH 9 measurement was different from critical or rejection limits of pH 4 and pH 10, respectively. Note that *s* for pH was underestimated, as statistics generated in this study were limited to one soil and did not include variability from soil heterogeneity or from field sampling, transport, and storage of soil. The accuracy of the method could be improved by reducing apparent systematic errors.

6.4.2 FM for minimum resistivity

In general, soil minimum resistivity measurements were relatively consistent across all 15 laboratories. All but two laboratories had an analog Nilsson 400 model resistivity meter and all but one laboratory used a four-pin measurement technique. Calibration checks with a resistor and with a conductivity standard were within 5% and 10%, respectively; likewise, little or no differences were seen when minimum resistivity measurements were checked with an audit meter. Summary statistics for laboratory visit minimum resistivity measurements were compared with those generated in the USF laboratory (Chapter 5, Section 5.3, Table 5-2). Although the data sets summarized in Table 6-3 were based on Santa Fe River soil collected from FDOT’s State Materials Office (SMO), soil sampling dates were November 11, 2013 for the USF laboratory results and March 10, 2014 for the laboratory visit results.

Table 6-3 Summary Statistics for Minimum Resistivity Measurements for a Sub-Sample of Air-Dried, Sieved, and Mechanically-Split Santa Fe River Soil

FM	N	Average, ohm-cm	St Dev (*s*), ohm-cm	%RSD	%RE
USF Laboratory	9	15,900	782	4.92	12.6
Laboratory Visits	15	24,000	2,840	11.9	41.7

For minimum resistivity, the average, standard deviation *s*, %RSD, and %RE were higher for laboratory visits than for the USF laboratory (Table 6-3). The higher average minimum resistivity may reflect in part heterogeneity of the stockpiled soil. Bias and thus accuracy remain undefined for a method in the absence of an accepted reference value, but a large %RE suggested the presence of systematic error. Refer to Table 6-4 for sources of variability in minimum resistivity measurements between laboratories.

Following the guidance of ASTM E177, example method statements of precision generated from the between-laboratory statistics were:

> Soil minimum resistivity measurements were made by 15 laboratories with randomly selected subsamples of an air-dried and sieved sandy soil. For a similar material, approximately 95% of individual test results from laboratories similar to those in the inter-laboratory study can be expected to differ in absolute value from their average by less than 2.0 x %RSD = 24%.
>
> Soil minimum resistivity measurements were made by 15 laboratories with randomly selected subsamples of an air-dried and sieved sandy soil. The average test value was 24,000 ohm-cm, and the reproducibility limit (between laboratory) was 2.8 x %RSD = 33%.

In practical terms, if the minimum resistivity average and standard deviation (laboratory visit *s* from Table 6-3) of the quality control and verification samples were 3,000 ± 360 (or ± 12%) ohm-cm, the null hypothesis (H_0) that the minimum resistivity was equal to 1,000 ohm-cm could be rejected at the 95% confidence level. These results suggested that the multi-laboratory precision for minimum resistivity was adequate with the caveat that statistics generated by this study were limited to one soil with a high minimum resistivity and did not include variability from soil heterogeneity or from field sampling, transport, and storage of soil.

Table 6-4 Sources of Variability in Minimum Resistivity between Laboratories

Soil stored at ambient temperatures or refrigerated
Soil tested at ambient temperatures or in a climate-controlled space (19 ^{o}C to 30 ^{o}C)
Used 250 g, 500 g, or 1000 g of soil and 10% water
Switched from 100 mL to 50 mL water when soil became saturated or used 100 mL for entire test
Tested soil "as is" or air dried
Used large or small soil box or homemade box
Mixed in containers of varying composition, size, and shape
Prepared soil with deionized or distilled water
Rinsed, partially rinsed, or did not rinse box between measurements
Added water with a resistivity ranging from 130,000 to >1,400,000 ohm-cm
Mixed with utensils or with hands (gloved and ungloved)
Filled box to a different level

An important factor in minimum resistivity measurements is soil temperature. ASTM G187 provides a model for correcting observed soil resistivity to a resistivity at a standard temperature (Chapter 3, Section 3.3.1, Equation 3-4). Soil minimum resistivity and corresponding temperature observations from laboratory visits were plotted with a least squares fit of the model to the data, which occurred for a standard temperature resistivity of 28,500 ohm-cm (Figure 6-1). Much of the data variability was not explained by the temperature model.

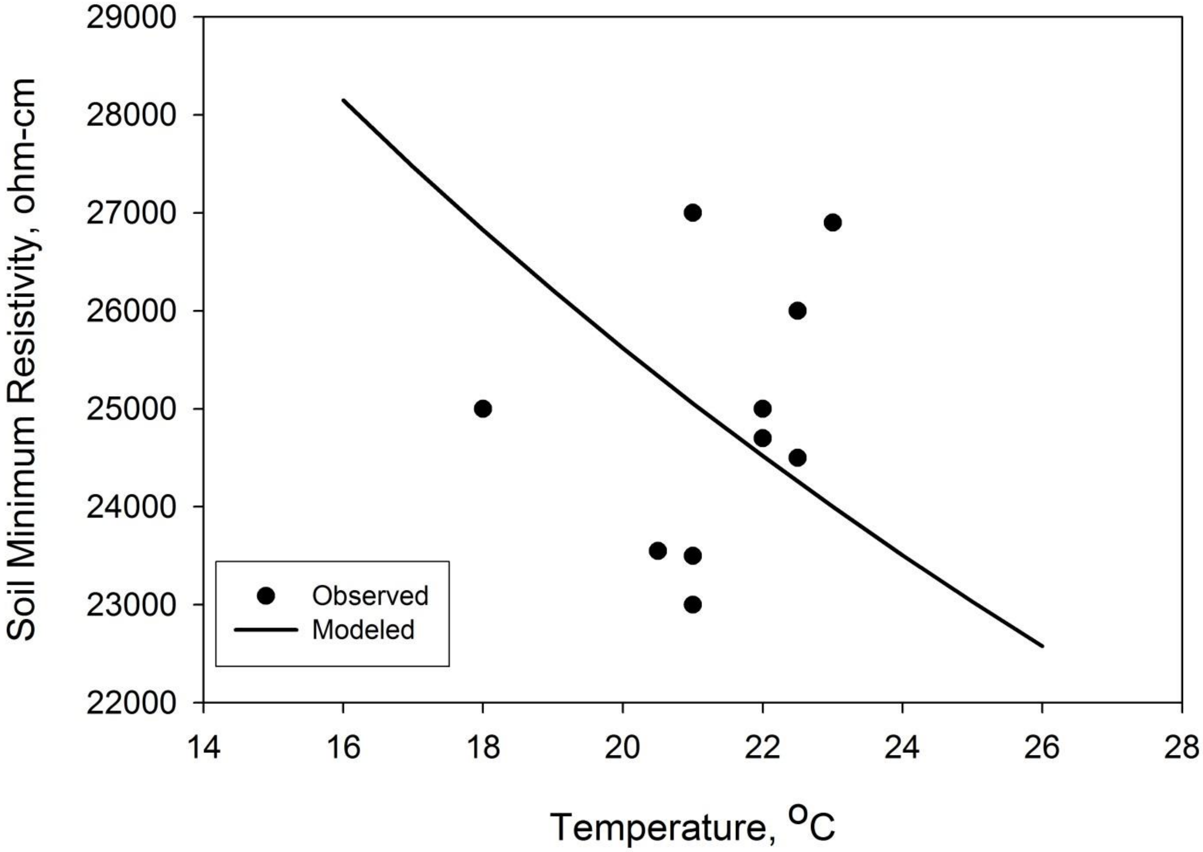


Figure 6-1. Modeled and observed soil minimum resistivity versus temperature.

Dilution water was a possible source of variability and its resistivity should be tested prior to making soil minimum resistivity measurements. In Figure 6-2 is shown soil minimum resistivity versus water resistivity. No clear trend was seen and the resistivity of most if not all of the laboratory water samples that were tested exceeded 200,000 ohm-cm.

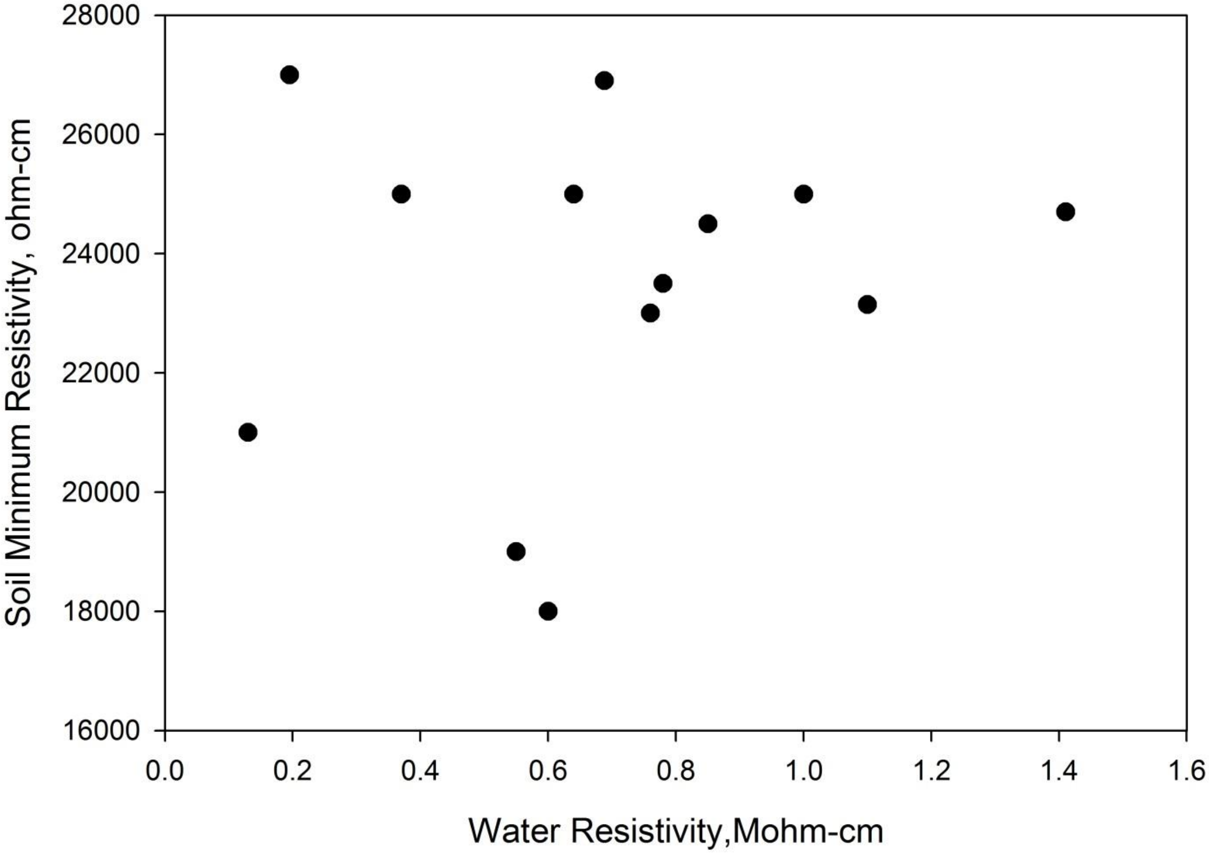


Figure 6-2. Observed soil minimum resistivity versus water resistivity.

In summary, for the average of two samples the multi-laboratory precision appeared adequate to assure that a measured minimum resistivity of 3,000 ohm-cm exceeded a rejection limit of 1000 ohm-cm, with the caveat that statistics generated in this study were limited to one soil with a high minimum resistivity and did not include variability from soil heterogeneity or from field sampling, transport, and storage of soil. The accuracy of the method could be improved by reducing apparent systematic errors.

6.4.3 FM for chloride

In general, measured chloride concentrations were in poor agreement across all 15 laboratories. Ten laboratories employed the Hach chloride low range test kit (5-400 ppm); four laboratories, the Hach chloride test kit with a digital titrator (10-10,000 ppm); and one laboratory a buret titration in accordance with SMEWW (Rice et al., 2012). Method procedures included steps to extract chloride from the soil with a 3:1 dilution using distilled water, followed by titration of chloride with silver nitrate in the presence of potassium dichromate. Silver chloride is relatively insoluble and so the chloride titration completes first and the dichromate titration second. As dichromate is titrated, the solution turns from a bright yellow to an orange-red. This color indicates the end point of the chloride titration. Lack of agreement in test results between laboratories were due in part to a difference in opinion regarding the intensity of the color at which the titration was completed and in part to the amount of sample titrated. The FDOT SMO laboratory was the only laboratory that tested the dilution water or a known chloride concentration to check their techniques and reagents. Summary statistics for chloride concentration measurements from the laboratory visits were compared with those generated in the USF laboratory through routine measurements of a 30-ppm check standard (Table 6-5). Test results were multiplied by three to mimic dilution of a soil extract.

Table 6-5 Summary Statistics for Measurements of a 30-ppm Chloride Standard*

FM 5-552 Chloride	*N*	Average, ppm	St Dev (*s*), ppm	%RSD	%RE
USF Laboratory	4	92	5	4.9	9.8
Laboratory Visits	15	140	48	35	120

*Test results were multiplied by 3 to mimic dilution of a soil extract

For chloride concentration, the average, standard deviation *s*, %RSD, and %RE were higher for laboratory visits than for the USF laboratory (Table 6-5). For the entire method, which includes soil sampling, transport, storage, extraction, and analysis, the bias and thus accuracy remain undefined in the absence of an accepted reference value, but a large %RE suggests the presence of systematic error. Refer to Table 6-6 for sources of variability in chloride concentrations between laboratories. Also included in this table were sources of variability from the soil extraction process, as the extraction process was described by method operators.

Following the guidance of ASTM E177, example method statements of precision generated from the inter-laboratory statistics were:

> Chloride concentration measurements were made by 15 laboratories with a 30-ppm standard chloride solution. Results were multiplied by three to mimic results for a diluted soil extract. For a soil with a 90-ppm chloride concentration, approximately 95% of individual test results from laboratories similar to those in the inter-laboratory study can be expected to differ in absolute value from their average by less than 2.0 x *s* = 95 ppm.
>
> Chloride concentration measurements were made by 15 laboratories with a 30-ppm standard chloride solution. Results were multiplied by three to mimic results for a diluted soil extract. The average test value was 136 ppm, and the reproducibility limit (between laboratory) was 2.8 x *s* = 140 ppm.

In practical terms, if the chloride concentration average and standard deviation of the quality control and verification samples were 100 ± 48 ppm, the null hypothesis (H_0) that the chloride concentration was equal to 500 ppm could be rejected at the 95% confidence level. These results suggested that the multi-laboratory precision for chloride is adequate, with the caveat that statistics generated by this study were limited to one 30-ppm check standard and did not include variability from soil extraction, soil heterogeneity or field sampling, transport, and storage of soil.

Table 6-6 Sources of Variability in Chloride Concentration between Laboratories

Mechanically split, quartered or thieved from original sample
Dried in oven at 60 ^{o}C or at 110 ^{o}C or in air at room temperature
Waited overnight to 8 days before filtering
Waited a few minutes to up to 5 days after filtering and before testing
Filtered with Fisher Q8, Fisher P9, Hach 132, Whatman 4, Whatman 41, or Whatman 42
Used two filters in sequence: Whatman 4 followed by Whatman 42
Filtered all of the sample or filtered water plus slurry or filtered water only
Filtered by gravity or filtered by suction
Filtered with a large or small funnel, or with a funnel made of plastic or glass
Removed filtrate by pipetting or by decanting
Filtered a split sample to speed filtration time
Based color change on a chart or on experience
Tested a soil extract volume of 10 mL or 23 mL or 40 mL or 100 mL (based on titrant concentration)

In summary, for the average of two samples the multi-laboratory precision appeared adequate to assure that an observed chloride concentration of 100 ppm did not exceed a rejection limit of 500 ppm, with the caveat that statistics generated in this study were limited to a chloride standard solution and did not include variability from soil extraction, soil heterogeneity, or field sampling, transport, and storage of soil. The accuracy of the method could be improved by reducing apparent systematic errors.

6.4.4 FM for sulfate

In general, measured sulfate concentrations were in poor agreement across all 15 laboratories. Five laboratories used a Hach photometer or spectrophotometer with a built-in sulfate calibration curve, another laboratory used a turbidimeter with a calibration curve prepared over a sulfate range of 10 to 120 ppm (Rice, 2012), and the nine remaining laboratories used a spectrophotometer such as but not limited to the Spectronics 20D+. For all but one of these nine laboratories, the conversion of % light transmission to sulfate concentration was based on a chart from an older version of FM for sulfate. Method procedures included steps to extract sulfate from the soil with a 3:1 dilution using distilled water, followed by reaction of a small volume of sample with barium chloride to form insoluble barium sulfate. The turbidity or light attenuation of the sample is proportional to its sulfate concentration. Lack of agreement between laboratories was due in part to a mismatch between the % transmission versus sulfate concentration relationship given by the chart and the actual response of the spectrophotometer. Other issues included measuring at a different wavelength, not using any calibration curve, and using the wrong reagent or out-of-date reagents. Only the FDOT SMO laboratory routinely tested a known sulfate concentration to check their techniques and reagents. Summary statistics for sulfate concentrations from the laboratory visits were compared with those generated in the

USF laboratory through routine measurements of a 30-ppm check standard (Table 6-7). The test results were multiplied by three to mimic dilution of a soil extract.

Table 6-7 Summary Statistics for Measurements of a 30-ppm Sulfate Standard[*]

FM	*N*	Average, ppm	St Dev (*s*), ppm	%RSD	%RE
USF Laboratory	5	88	8	9.5	24
Inter-Laboratory	15	100	35	34	150

[*] Test results were multiplied by 3 to mimic dilution of a soil extract.

For sulfate concentration, the average, standard deviation *s*, %RSD, and %RE were higher for laboratory visits than for the USF laboratory (Table 6-7). For the entire method, which includes soil sampling, transport, storage, extraction, and analysis, the bias and thus accuracy remain undefined in the absence of an accepted reference value, but a large %RE suggests the presence of systematic error. Refer to Table 6-8 for sources of variability in sulfate concentrations between laboratories. Refer to Table 6-6 for sources of variability from the soil extraction process, as the extraction process was described by method operators.

Following the guidance of ASTM E177, example method statements of precision generated from the inter-laboratory statistics were:

> Sulfate concentration measurements were made by 15 laboratories with a 30-ppm standard sulfate solution. Results were multiplied by three to mimic results of a diluted soil extract. For a soil of similar concentration, approximately 95% of individual test results from laboratories similar to those in the inter-laboratory study could be expected to differ in absolute value from their average by less than $2.0 \cdot s = 70$ ppm.
>
> Sulfate concentration measurements were made by 15 laboratories with a 30-ppm standard sulfate solution. Results were multiplied by three to mimic results of a diluted soil extract. The average test value was 103 ppm, and the reproducibility limit (between laboratory) was $2.8 \cdot s = 99$ ppm.

In practical terms, if the sulfate concentration average and standard deviation of the quality control and verification samples were 100 ± 35 ppm, the null hypothesis (H_0) that the sulfate concentration was equal to the rejection limit of 1000 ppm could be rejected at the 95% confidence level. These results suggested that the multi-laboratory precision for sulfate was adequate, with the caveat that statistics generated by this study were limited to one 30 ppm-check standard and did not include variability from soil extraction, soil heterogeneity, or field sampling, transport, and storage of soil.

Table 6-8 Sources of Variability in Sulfate Concentrations between Laboratories

Added HCl different amounts, concentrations, and to different sample volumes, if added
Chose a different Hach photometer range (range 1 or range 2) for built-in curve
Used a turbidity (light scattering) instead of a light attenuation measurement
Added a buffer to stabilize barium sulfate precipitate
Checked and adjusted pH before testing
Shook reaction tube either gently or vigorously
Reacted and measured sulfate in same tube or reacted in one tube and transferred to a cuvette for measurement
Used distilled water for a blank or used an unreacted sample
Converted from light attenuation to sulfate by % transmission vs sulfate chart in older version of FM or by built-in sulfate curves prepared by Hach or by other calculation
Made measurement at 360 nm or 420 nm or 470 nm
Diluted sample by 1:9 or 1:99 when needed; diluted in a flask or in a reaction tube

In summary, for the average of two samples the multi-laboratory precision appeared adequate to assure that an observed sulfate concentration of 200 ppm did not exceed a rejection limit of 1000 ppm, with the caveat that statistics generated in this study were limited to a sulfate standard solution and did not include variability from soil extraction, soil heterogeneity, or field sampling, transport, and storage of soil. The accuracy of the method could be improved by reducing apparent systematic errors.

6.5 Summary

Results of laboratory visits suggested that for pH, analysis of more than two independent samples may be necessary to distinguish an observed pH at the acceptance limits of pH 5 or 9 from the corresponding pH rejection limits of pH 4 or 10. For minimum resistivity, chloride, and sulfate, two independent samples were adequate to distinguish an observation at the acceptance limit from the rejection limit. The caveats for these results were (1) hypothesis testing included Type I (α) error but not Type II (β) error; and (2) statistics generated in this study were limited to a test soil and standard solutions and did not include variability from soil extraction, soil heterogeneity, or field sampling, transport, and storage of soils. The accuracy of all methods could be improved by reducing apparent systematic errors.

7 Soil Sampling of Select Backfill

7.1 Introduction

In this chapter were described field sampling protocols for soils collected for ruggedness, treatment, and other factor analysis studies (Chapters 8 and 9), where field sampling was used in the broadest sense to include sample collection, transport, and storage. Also in this chapter were summarized the geotechnical properties of the all soils tested and the results of split sample analyses.

7.2 Field Sampling of Select Backfill

In addition to select backfill collected from bins at FDOT's SMO, samples of backfill material were also collected from eight mines, seven of which were in FDOT's Districts 1 and 7 and one of which was in District 5. Refer to Table 1-1 (Chapter 1, Section 1.2.7) for summary of the mine owners, locations, and sampling dates.

The Transcor Dirt Services mine (Mine 1) was an open pit with fine sands that ranged in color from white to reddish yellow to dark brown. A backhoe operator dug 12 holes about 3-m deep in a grid pattern with holes spaced roughly 50 m apart. Sand samples of ~25 kg were collected in buckets from each of the excavated dirt piles, and these buckets were transported to a nearby nylon tarp. Sands in the buckets were emptied onto the tarp and mixed by rolling the tarp. Once the sands were mixed, subsamples were acquired and divided into buckets or sealable plastic bags for transport under ambient conditions or in a cooler on ice, respectively, to the USF soils laboratory. One ~3-kg sub-sample was placed in sealable plastic bag for on-site analyses and two ~3-kg subsamples were placed in sealable plastic bags and transported in coolers on ice for split-sample analyses by local laboratories.

The Jahna Industries (Mine 2), Youngquist Brothers Rock (Mine 3), Angelo's Recycled Material (Mine 5), Titan (Mine 7) and Cemex (Mine 8) mines had stockpiles of backfill; the Calhoun (Mine 4) and Hickey Excavating (Mine 6) mines were sand pits but the sampling protocol was the same. Mine 2 and Mine 7 samples were classified by the mine owners as "mason's sand"; Mine 8 samples came from a tailings stockpile. At each of these mines an equipment operator removed one front loader bucket of sand from three separate locations near the base of the stockpile or pit. The three loads were kept separate but placed one next to the other. Four sand samples of ~12 kg were collected in buckets from each of the excavated piles, and these buckets were carried to a nearby nylon tarp. Sands in the buckets were emptied onto the tarp and mixed by rolling the tarp. Once the sands were mixed, subsamples were acquired and divided into buckets or sealable plastic bags for transport under ambient conditions or in a cooler on ice, respectively, to the USF soils laboratory. One ~3-kg sub-sample was placed in a sealable plastic bag for on-site analyses and one or two ~3-kg subsamples were placed in sealable plastic bags and transported in a cooler on ice for split-sample analyses by an FDOT or commercial laboratory. For samples from Mines 1 through 4, on-site analyses included measurement in triplicate of backfill pH and resistivity; for Mines 5 through 8, pH and conductivity. Samples brought back to the USF soils laboratory were processed for geotechnical testing and ruggedness, treatment and other factor analysis studies, with subsamples separated for storage in a refrigerator or at room temperature and air- or oven-dried, as necessary, for each study.

7.3 Geotechnical Properties of Select Backfill

Geotechnical testing was performed in the USF soils laboratory. The methods employed were AASHTO T88 for particle size analysis (not including the hydrometer test), AASHTO T89 for liquid limit, AASHTO T90 for plasticity limit (hand rolling technique), AASHTO T265 for moisture content, and AASHTO T267 for organic matter content. Refer to Table 7-1 for a summary of the geotechnical properties of the sand mine samples. The names given to backfill samples were for project use only and were not related to U. S. Geological Survey or U. S. Department of Agriculture soil names. All of the listed samples were classified as sand (AASHTO soil classification A-3) and all samples met the geotechnical requirements for select backfill (Chapter 2, Section 2.1.2).

Table 7-1 Geotechnical Properties of Select Backfill Samples

Mine ID	Backfill Name	Liquid Limit	Plasticity Index	% Passing #200 Sieve	% Organic Matter
SMO	Starvation Hill	NP	NP	2.00	0.37
SMO	Santa Fe	NP	NP	3.03	0.67
1	Wimauma	NP	NP	2.10	0.53
2	Jahna	NP	NP	2.21	0.08
3	Youngquist	NP	NP	5.81	0.60
4	Calhoun	NP	NP	3.41	0.34
5	Angelo’s	NP	NP	6.10	1.07
6	Sebring	NP	NP	4.64	0.47
7	Clermont	NP	NP	0.74	0.07
8	Alico Road	NP	NP	3.40	0.81

7.4 Split Sample Analyses

Results from split sample analyses were shown in Table 7-2. The USF results were the averages obtained across two or more treatments (Chapter 9, Section 9.1).

Table 7-2 Results for Laboratory Analysis of Split Samples

Laboratory	pH	Minimum Resistivity, ohm-cm	Soil Chloride, ppm	Soil Sulfate, ppm
Mine 1Wimauma				
Laboratory 2	4.6	42,000	30	21
Laboratory 5	4.9	42,000	15	6
USF*	4.7	44,700	BD	10
Mine 2 Jahna				
Laboratory 4	7.8	19,000	85	73
USF*	5.2	116,000	BD	BD
Mine 3 Youngquist				
Laboratory 1	8.1	6,100	30	118
Laboratory 2	8.0	5,500	31	81
USF*	8.2	9,150	BD	36
Mine 4 Calhoun				
Laboratory 3	5.1	31,000	9	BD
USF*	4.6	104,000	BD	BD
Mine 5 Angelo’s				
Laboratory 6	5.6	27,000	113	30
USF*	4.6	17,800	BD	24
Mine 6 Sebring				
Laboratory 3	5.0	38,000	6	12
USF*	4.4	36,100	BD	16
Mine 7 Clermont				
Laboratory 6	8.0	19,700	34	21
USF*	7.5	28,200	BD	BD
Mine 8 Alico Road				
Laboratory 1	8.9	24,000	15	79
USF*	9.0	11,200	BD	BD

*Results were averaged across all treatments (Chapter 9, Table 9-1) and rounded for ease of comparison.
BD = below detection

For pH, agreement between laboratories was within 0.5 pH units for Wimauma, Youngquist, Calhoun, Clermont, and Alico Road sands, within 0.6 pH units for Sebring sand, 1 pH unit for Angelo’s sand, and 2.6 pH units for Jahna sand (Table 7-2). For divergent pH values, USF results were lower than partnered laboratories (Table 7-2). For samples for Mines 5 through 8, USF trialed the use of KCl addition to soil solutions prepared for pH measurement. The addition of KCl tends to lower the sample pH by as much as 0.5 pH units. Among the eight soils, four soils had at least one pH result below the acceptance limit of pH 5.

For minimum resistivity, between-laboratory agreement was reasonable for three sands: Wimauma, Youngquist, and Sebring (Table 7-2). For Jahna and Calhoun sands, USF reported much higher values than the partnered laboratory (Table 7-2). USF trialed a change to the FM between Mines 1 through 4 and Mines 5 through 8; for samples from the latter four mines the water was decanted first into soil box from the soil slurry that formed with the addition of water. This change brought the between-laboratory results at least to the same measurement scale. No reported minimum resistivity approached the acceptance limit of 3000 ohm-cm.

For chloride, USF reported that all concentrations were below detection. For the commonly-used Hach chloride test kits, the stated method detection level is 5 ppm (15 ppm if multiplied by a dilution factor of 3 to obtain soil concentration). For these chloride measurements, USF trialed two changes to the FM: the first change was to remove suspended particles and most, if not all, of the color in the sand extract prior to testing for chloride; the second change was to test the dilution water and to subtract the dilution water chloride concentration from the chloride concentration of the sample extract. Reducing the potential for interference may explain in part the below-detection results obtained by USF. From Table 7-2, between-laboratory chloride concentrations diverged for Jahna and Angelo’s sands, and one result for Angelo’s sand exceeded the acceptance limit of 100 ppm.

For sulfate, USF reported that four concentrations were below detection. For the Hach photometer kit, which was not in routine use, the stated detection level is 2 ppm (6 ppm if multiplied by a dilution factor of 3 to obtain soil concentration). For these sulfate measurements, USF trialed a change to the FM to remove suspended particles and most, if not all, of the color in the sand extract prior to testing for sulfate. Reducing the potential for interference may explain in part the below-detection results obtained by USF. From Table 7-2, agreement in sulfate concentration between laboratories was reasonable for Wimauma, Calhoun, Angelo’s, Sebring, and Clermont sands but diverged for Alico Road, Youngquist, and Jahna sands. No reported sulfate concentration exceeded the acceptance limit of 200 ppm.

Differences in method procedures between laboratories aside, across eight sands, four sands—Wimauma, Calhoun, Angelo’s, and Sebring—failed to meet the acceptance limit for one or more of the corrosion properties. For Wimauma sand, three laboratories agreed on the failed acceptance limit, but for the other three sands, the failure was in dispute. If the split sample analyses between two laboratories represented quality control and verification tests, at least three out of the eight sands would require resolution testing. Reduction in a relatively high rate of resolution testing may offset additional costs associated with method improvements.

7.5 Summary

Divergence in corrosion test results between laboratories was seen for pH, minimum resistivity, chloride, and sulfate for one or more of the eight sands collected from mines as part of this study. Changes to the FMs for minimum resistivity, chloride, and sulfate that were trialed by USF showed promise for improving between-laboratory agreement. Split sample analyses revealed that four of the eight sands failed to meet an acceptance limit for one more of the corrosion properties in one or more of the partnered laboratories. If the split sample analyses between two laboratories represented quality control and verification tests, at least three out of the eight sands would require resolution testing. Reduction in a relatively high rate of resolution testing may offset additional costs associated with method improvements.

8 Ruggedness Studies

8.1 Overview

A ruggedness study is a tool to examine how robust a method is to small changes in equipment, procedures, materials, and environmental factors, as examples, which simulates differences in method performance that might be expected between laboratories and anticipates the method precision or reproducibility. Ideally, a ruggedness study precedes release of a new or revised method for an inter-laboratory study; in this case, however, the ruggedness study also serves as a baseline for evaluating potential changes to a current method.

Ruggedness studies were first conducted with Santa Fe River soil prior to laboratory visits (Chapter 6) to explore sensitivity of results to anticipated variations in method procedures (Section 8.2). Soil samples were dried, sieved, and stored prior to use and as such did not represent fully soils that were freshly acquired from a pit but serve better as examples for later studies.

Transport, storage, and processing conditions were included as factors for the second round of ruggedness studies (Section 8.3). Refer to Chapter 7, Section 7.2, for a description of the sampling protocols. These studies followed the laboratory visits (Chapter 6) and were expanded to evaluate procedural differences between laboratories, between AASHTO and FMs, and between current and proposed FMs. The ruggedness study worked well for identifying changes in procedural steps that have a strong influence on the results, but at the same time, the presence of a strong influence worsened the method's relative precision and bias, and in effect, swamped the roles of less influential factors. Factor analysis studies such as the treatment studies (Chapter 9) explored further changes to procedural steps that had a strong influence.

For all ruggedness studies, statistical significance of factor effects was determined by *t*-tests for averages and *F*-tests for standard deviations between related factors at the 95% confidence level ($p < 0.05$).

8.2 Ruggedness Study for Santa Fe River Soil

8.2.1 Summary results

Summary statistics for ruggedness studies with Santa Fe River soil are presented in Table 8-1 and are discussed in more detail with respect to each method. Sodium chloride and sodium sulfate were added to the soil to achieve detectable chloride and sulfate concentrations but still have a minimum resistivity above 3,000 ohm-cm; the pH ruggedness studies were done for soils with and without added salt.

Table 8-1 Summary Statistics for Ruggedness Studies with Santa Fe River Soil

Statistic	Unmodified	Amended with 0.10 g/kg NaCl and 0.10 g/kg Na_2SO_4			
	pH	pH	Min Resistivity (ohm-cm)	Chloride (ppm)	Sulfate (ppm)
Average	8.09	7.91	3,540	50	142
St Dev	0.18	0.13	290	12	62
%RSD	2.27	1.70	8.20	23.5	44.0
%RE	6.18	4.30	22.6	63.0	145

8.2.2 FM for pH

The pH ruggedness study included both refrigerated and non-refrigerated samples to evaluate the effect of temperature change. To evaluate the effect of ionic strength, the equilibration time was varied, as was the water-to-soil ratio, the use of distilled versus deionized water (distilled water had a higher conductivity), and the degree of sample stirring; moreover, the study was repeated with salt amendment, which raised the sample ionic strength. To evaluate the effect of electrode condition, two electrodes with acceptable but different offsets were tested. Also tested was the measurement geometry (height of water above the sample) between a beaker and flask. Factors and pH determinations are presented in Table 8-2.

To assess the effect of a change from the original, for each factor the average of the change is subtracted from the average of the original (Youden, 1975). With this approach and according to the test matrix, all other factors appear twice on each side of the calculation and are thus canceled out. For example, in the measurement of pH (Table 8-2), the effect of using 100 g instead of 100 mL of unmodified soil is calculated as ((7.99 + 8.01 + 7.90 + 8.18) / 4) - ((7.94 + 8.40 + 8.00 + 83.1) / 4) = - 0.14; interestingly, the effect is lessened with the addition of salt to the sample: ((7.86 + 7.98 + 7.75 + 8.00 + 8.09) / 4) - (8.09 + 7.75 + 8.04 + 7.81)/4) = -0.025. To estimate the method reproducibility s_R, the standard deviation of the eight results was calculated. For pH, the standard deviations were 0.18 pH unit and 0.13 pH unit for unmodified and salt-amended soils, respectively (Table 8-1).

Table 8-2 Ruggedness Study for pH

Factors		Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	ML	ML	ML	ML	G	G	G	G
B	b	RT	RT	C	C	RT	RT	C	C
C	c	30	0	30	0	30	0	30	0
D	d	DS	DS	DI	DI	DI	DI	DS	DS
E	e	1	2	1	2	2	1	2	1
F	f	GS	NS	NS	GS	GS	NS	NS	GS
G	g	wet	dry	dry	wet	dry	wet	wet	dry
pH (unmodified; wetted/dry soil)		7.99	8.01	7.90	8.18	7.94	8.40	8.00	8.31
pH (salt-amended; beaker/flask)		7.86	7.98	7.75	8.00	8.09	7.75	8.04	7.81

A	100 mL soil (ML)
a	100 g soil (G)
B	Room temperature sample (RT)
b	Cold sample (taken directly from the refrigerator at 4 ^{o}C) (C)
C	30-min equilibration (30)
c	No equilibration (0)
D	Mixed with distilled water (DS)
d	Mixed with deionized water (DI)
E	pH electrode 1 (1)
e	pH electrode 2 (2)
F	Gently stirred (GS)
f	Not stirred (NS)
G	Wetted overnight (wet) or tested in beaker
g	Kept dry (dry) or tested in flask

For the unmodified soil, the pH average, standard deviation, %RSD, and %RE were 8.09, 0.18, 2.27%, and 6.18%, respectively (Table 8-1); for the salt-amended soil they were 7.91, 0.13, 1.70%, and 4.30%. Note that the addition of sodium salts lowered the average pH by 0.18 pH units. The effect of factors on pH measurement was summarized in Table 8-3 and Table 8-4 for unmodified and salt-amended Santa Fe River soils, respectively. For the unmodified soil, the pH average was significantly higher when pH was measured without delay than after a 30-min equilibration (Table 8-3). One explanation is that a 30-min equilibrium period raised the solution ionic strength compared with no equilibrium period. For the unmodified soil, no other factors had a significant effect either on the average or standard deviation soil pH (Table 8-3). For the salt-amended soil, the pH average was significantly higher when pH was measured with electrode 2 rather than electrode 1, possibly due to differing responses of the electrode liquid junctions to ionic strength. For the salt-amended soil, no other factors had a significant effect either on the average or standard deviation soil pH (Table 8-4).

Table 8-3 Effect of Factors in pH Ruggedness Study for Unmodified Santa Fe River Soil

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH was higher if sample
A	8.020	0.117				Water-to-soil ratio was higher
a	8.163	0.227	-0.143	0.306	0.306	
B	8.085	0.212				Was colder
b	8.098	0.183	-0.012	0.814	0.932	
C	7.958	0.046				Measured without delay
c	8.225	0.169	-0.267	0.061	0.023	
D	8.078	0.155				Diluted with deionized water
d	8.105	0.232	-0.027	0.525	0.850	
E	8.150	0.242				Measured with electrode 1
e	8.033	0.103	0.118	0.194	0.407	
F	8.105	0.171				Was gently stirred
f	8.078	0.221	0.027	0.688	0.850	
G	8.143	0.193				Wetted overnight
g	8.040	0.186	0.102	0.953	0.473	

Table 8-4 Effect of Factors in pH Ruggedness Study for Salt-Amended Santa Fe River Soil

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH was higher if sample
A	7.898	0.116				Water-to-soil ratio was higher
a	7.923	0.168	-0.025	0.562	0.814	
B	7.920	0.147				Was warmer
b	7.900	0.142	0.020	0.951	0.851	
C	7.935	0.158				Measured after 30 min
c	7.885	0.124	0.050	0.700	0.636	
D	7.923	0.106				Diluted with distilled water
d	7.898	0.174	0.025	0.436	0.814	
E	7.793	0.053				Measured with electrode 2
e	8.028	0.049	-0.235	0.886	0.001	
F	7.940	0.128				Was gently stirred
f	7.880	0.152	0.060	0.787	0.569	
G	7.913	0.133				Was tested in a beaker
g	7.908	0.156	0.005	0.801	0.963	

Recall that for Santa Fe River sand tested during laboratory visits the %RSD and %RE for pH were 10.1% and 32.4%, respectively (Chapter 6, Section 6.4.1, Table 6-1) compared with the ruggedness study results shown in Table 8-3 of 2.27% and 6.18% for the same statistics, respectively. Thus, this ruggedness study for pH did not introduce the variability in pH seen in the laboratory visits, which was likely dominated by electrode failure.

In summary, the FM for pH was sensitive to a 30-min equilibration of the soil versus no equilibration period; when the soil was amended with salt this sensitivity disappeared and the improvement in precision and bias revealed a significantly different pH response by electrode. These results suggested that soil ionic strength, equilibration period, and electrode condition were factors important method bias and precision.

8.2.3 FM for minimum resistivity

The ruggedness study for resistivity included both refrigerated and non-refrigerated samples to evaluate the effect of temperature change. To evaluate the effect of ionic strength, an overnight wetting period was introduced, as were changes in the water-to-soil ratio and the use of distilled versus deionized water (distilled water had a higher conductivity). Matched and unmatched test leads were compared as unmatched leads likely add resistance to a balanced bridge resistance measurement; a change in incremental water volume was compared as smaller volumes might better locate the minimum resistance; and small and large soil boxes were compared as a larger box might better describe soil heterogeneity. Factors and minimum resistivity determinations were presented in Table 8-5.

Table 8-5 Ruggedness Study for Minimum Resistivity

Factors		Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	1000	1000	1000	1000	750	750	750	750
B	b	RT	RT	C	C	RT	RT	C	C
C	c	100	75	100	75	100	75	100	75
D	d	DS	DS	DI	DI	DI	DI	DS	DS
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	dry	wet	wet	dry	dry	wet	wet	dry
G	g	M	UM	UM	M	UM	M	M	UM
Minimum Resistivity (ohm-cm)		3500	3250	3900	3400	3250	3500	4050	3450

A	1000 g soil (1000)
a	750 g soil (750)
B	Room temperature sample (RT)
b	Cold sample (taken directly from the refrigerator at 4 °C) (C)
C	100 mL water increments (100)
c	75 mL water increments (75)
D	Mixed with distilled water (DS)
d	Mixed with deionized water (DI)
E	Small soil box (SM)
e	Large soil box (LG)
F	Dry soil (dry)
f	Soil wetted overnight (wet)
G	Matched wire (M)
g	Unmatched wires (UM)

For this ruggedness study, the soil minimum resistivity average, standard deviation, %RSD, and %RE were 3,540 ohm-cm, 290 ohm-cm, 8.20%, and 22.6%, respectively (Table 8-1). From the resistivity ruggedness study, the effects of factor perturbations were seen in the differences of average resistivity between the original and change, which were summarized in Table 8-6 for salt-amended Santa Fe River soil. No factors had a significant effect either on the average or standard deviation soil minimum resistivity (Table 8-6).

Table 8-6 Effect of Factors in Minimum Resistivity Ruggedness Study for Salt-Amended Santa Fe River Soil

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Minimum resistivity was higher if
A	3,513	278				Mass (weight) of sample was lower
a	3,563	342	-50	0.740	0.828	
B	3,375	144				Sample was colder
b	3,700	324	-325	0.217	0.117	
C	3,675	366				For 100 mL increments of water
c	3,400	108	275	0.075	0.200	
D	3,563	342				Diluted with distilled water
d	3,513	278	50	0.740	0.828	
E	3,588	210				Measured with small soil box
e	3,488	382	100	0.352	0.662	
F	3,400	108				Sample was wetted overnight
f	3,675	366	-275	0.075	0.200	
G	3,613	295				If test leads were matched
g	3,463	307	150	0.953	0.507	

Recall that from the laboratory visits (Chapter 6, Section 6.4.2, Table 6-3) for Santa Fe River sand the %RSD and %RE for minimum resistivity were 11.9%, and 41.7%, respectively, compared with the ruggedness study results shown in Table 8-5 of 8.2% and 22.6% for the same statistics, respectively. This ruggedness study for minimum resistivity did not capture the variability seen in laboratory visits.

8.2.4 FM for chloride

Factors for a ruggedness study for chloride included changes from the original FM in the amount of chloride tested (soil mass, amount of sample), sample clarity (settling time, use of membrane filtration, portion of extract that was filtered), and potential interferences (distilled versus deionized water and stirring technique). Factors and chloride concentration determinations are presented in Table 8-7.

Table 8-7 Ruggedness Study for Soil Chloride Concentration

Factors		Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	100	100	100	100	75	75	75	75
B	b	24	24	48	48	24	24	48	48
C	c	HI	LO	HI	LO	HI	LO	HI	LO
D	d	DS	DS	DI	DI	DI	DI	DS	DS
E	e	N	Y	N	Y	Y	N	Y	N
F	f	ALL	100	100	ALL	ALL	100	100	ALL
G	g	HS	MS	MS	HS	MS	HS	HS	MS
Chloride Concentration (ppm)		68	57	50	65	42	43	41	36

A	100 g dried, sieved soil (100)
a	75 g dried, sieved soil (75)
B	24 hr of settling (24)
b	48 hr of settling (48)
C	High range for 0.22 N $AgNO_3$ test (40 mL sample) (HI)
c	Low range for 0.22 N $AgNO_3$ test (100 mL sample) (LO)
D	Distilled water (DS)
d	Deionized water (DI)
E	No membrane filtration (N)
e	Filtration with a 0.45 micron mixed cellulose ester filter (Y)
F	Filter all of the extract (ALL)
f	Filter the first 100 mL of extract (100)
G	Hand swirl sample (HS)
g	Machine stir sample (MS)

For this ruggedness study, the soil chloride concentration average, standard deviation, %RSD, and %RE were 50 ppm, 12 ppm, 23.5%, and 63.0%, respectively (Table 8-1). Only one factor—a change in soil mass—had a significant effect on average chloride concentration (Table 8-8). The sensitivity of the method to soil mass suggests that the accuracy of chloride analysis would be worsened for measurements made in the field versus in a laboratory, because in the field soil mass would vary with volumetric measures and field moisture content. No factors had a significant effect on the standard deviation of chloride concentration (Table 8-8).

Table 8-8 Effect of Factors in Chloride Ruggedness Study for Salt-Amended Santa Fe River Soil

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Chloride concentration was higher if
A	60	8				Mass (weight) of sample was higher
a	40	3	19	0.141	0.004	
B	52	12				Settling time was lower
b	48	13	5	0.967	0.613	
C	50	12				(No difference based on sample size)
c	50	13	0	0.938	0.984	
D	50	15				(No difference based on water type)
d	50	10	1	0.594	0.952	
E	49	14				Filtered through a membrane
e	51	12	-2	0.814	0.825	
F	53	16				All the extract was filtered
f	47	7	5	0.246	0.584	
G	54	14				Titrated sample was hand-swirled
g	46	9	8	0.488	0.396	

In the execution of the ruggedness study for chloride concentration, a few problems with the digital titrator were noted. First, the titrator mechanism that facilitates a quick removal of the titrant cartridge did not function, which made cartridge removal a *very* time-consuming task. The titrant degrades faster if exposed to light, and the titrant cartridge should be capped and returned to its box after each use to prevent this exposure. In lieu of this, the installed cartridge was covered with aluminum foil. Second, at times when dialing the digits from 9 to 10 or 99 to 100, the digit in the tenth or 100th place, respectively, did not turn over, causing an undercounting of digits by at least 10 digits. Finally, the delivery tube seemed to leak a small but continuous stream of titrant, which grew stronger with stirring. This too, would cause an undercounting of digits and results in a lower estimate of the soil chloride concentration. Combined, these problems contributed to noise in the chloride analyses.

Recall that from the laboratory visits (Chapter 6, Section 6.4.3, Table 6-5) for a 30-ppm aqueous chloride standard, the %RSD and %RE for chloride concentration were 35.1%, and 115%, respectively, compared with the ruggedness study results shown in Table 8-7 of 23.5% and 63.0% for the same statistics, respectively. Thus, this ruggedness study for chloride did not capture the variability seen in the laboratory visits.

In summary, the FM for chloride was sensitive to soil mass tested, which suggested that drying the soil to a constant mass is an important method step. Also noted were issues with the digital titrator that make it unsuitable for a standard test method.

8.2.5 FM for sulfate

Factors for a ruggedness study for sulfate included to changes from the original FM in the amount of sulfate tested (soil mass), sample clarity (settling time, use of membrane filtration, acid addition, portion of extract that was filtered), and potential interferences (distilled versus deionized water and timing of analysis). Factors and sulfate concentration determinations were presented in Table 8-9. Soil samples were diluted by a factor of three (3:1 water-to-soil ratio), but an additional factor of two dilution of the filtered soil extract was necessary to obtain a reading on the Hach photometer, as the range on the custom calibration curve was from 0 to 40 ppm as sulfate. Thus, any error in the photometer reading was inflated by a factor of six.

Table 8-9 Ruggedness Study for Soil Sulfate Concentration

Factors		Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	100	100	100	100	75	75	75	75
B	b	48	48	24	24	48	48	24	24
C	c	N	Y	N	Y	N	Y	N	Y
D	d	DS	DS	DI	DI	DI	DI	DS	DS
E	e	N	Y	N	Y	Y	N	Y	N
F	f	ALL	100	100	ALL	ALL	100	100	ALL
G	g	5	10	10	5	10	5	5	10
Sulfate Concentration (ppm)		228	132	204	132	138	168	132	114

A	100 g dried, sieved soil (100)
a	75 g dried, sieved soil (75)
B	24 hr of settling (24)
b	48 hr of settling (48)
C	No membrane filtration (N)
c	Filtration with a 0.45 micron mixed cellulose ester filter (Y)
D	Distilled water (DS)
d	Deionized water (DI)
E	No added acid (N)
e	Added acid (Y)
F	Filter all of the extract (ALL)
f	Filter the first 100 mL of extract (100)
G	Test at 5 min (5)
g	Test at 10 min (10)

For this ruggedness study, the soil sulfate concentration average, standard deviation, %RSD, and %RE were 142 ppm, 62 ppm, 44.0%, and 145%, respectively (Table 8-1). Compounded by dilution error, large swings in concentration seen for sample mass (Factors A, a), acid addition (Factors E, e), and test interval (Factors G, g) contributed to high %RSD and %RE. Average sulfate concentrations were not significantly higher for any factor, but sulfate concentration standard deviation was significantly higher when soil extracts were not filtered through a membrane (Table 8-10). These results emphasized the need to further clarify sample extracts before sulfate testing. Although not statistically significant, another relatively large but expected effect was noted for soil mass: sulfate concentration was 65 ppm higher when 100 g versus 75 g were extracted (Table 8-10). The sensitivity of the method to soil mass suggested that the accuracy of sulfate analysis would be worsened for measurements made in the field versus in a laboratory, because in the field soil mass would vary with volumetric measures and field moisture content.

Table 8-10 Effect of Factors in Sulfate Ruggedness Study for Salt-Amended Santa Fe River Soil

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Sulfate concentration was higher if
A	174	49				Mass (weight) of sample was higher
a	109	62	65	0.725	0.153	
B	138	86				Settling time was longer
b	146	40	-8	0.238	0.876	
C	147	92				Not filtered through a membrane
c	137	23	10	0.046	0.836	
D	152	52				Extracted with distilled water
d	132	78	20	0.514	0.688	
E	179	50				No acid was added
e	105	55	74	0.880	0.092	
F	124	84				First 100 mL of extract was filtered
f	159	34	-35	0.177	0.473	
G	165	45				Tested at 5 min
g	118	74	47	0.436	0.325	

With the Hach photometer, a custom calibration curve proved difficult to prepare and maintain because (1) sulfate concentrations prepared in 5 ppm increments often had the same absorbance reading, and (2) even with 10-ppm increments, curves were not linear over the target range. Performance of the photometer's built-in calibration curve is discussed in Chapter 9 (Section 9.2).

Recall that from the laboratory visits (Chapter 6, Section 6.4.4, Table 6-7) for a 30-ppm aqueous sulfate standard the %RSD and %RE for sulfate were 34.1%, and 146%, respectively, compared with the ruggedness study results shown in Table 8-9 of 44% and 145% for the same statistics, respectively. Thus, this ruggedness study for sulfate mimicked the variability seen in the laboratory visits.

In summary, for the FM for sulfate the soil mass and extract clarity were factors that potentially but not conclusively contributed to measurement bias and precision. Moreover, the accuracy of the photometer-based measurement was limited due to the non-linearity of the calibration curve.

8.3 Ruggedness Studies for Mined Soils

8.3.1 Summary statistics

Ruggedness studies were accomplished for pH and resistivity on all eight sands, sulfate concentration on four sands, but chloride concentration on no sands. Refer to Appendix A for ruggedness study factors, determinations, and statistical significance, which were tabulated by sand and by method. Transport, storage, and processing conditions were included as factors in the ruggedness studies; note, however, that for pH and resistivity, refrigerated samples were brought to room temperature before testing. Samples processed for sulfate analyses were oven-dried and stored at room temperature. The overall average, standard deviation, % relative standard deviation (%RSD), and % relative error (%RE) for each study were summarized in Table 8-11. Note that these statistics were suggestive of the method reproducibility to the extent that the chosen factors and their variability capture the variability that occurs between laboratories.

Table 8-11 Summary Statistics for Ruggedness Study Results

Statistic	pH	Minimum Resistivity, ohm-cm	Chloride Concentration, ppm	Sulfate Concentration, ppm
Mine 1 Wimauma Sand				
Avg	4.65	52,400	Below detection	24
St Dev	0.19	7,790		13
% RSD	4.05	14.9		55
% RE	11.0	42.0		163
Mine 2 Jahna Sand				
Avg	4.72	147,000	Not tested	Not tested
St Dev	0.12	19,300		
% RSD	2.64	13.1		
% RE	8.27	40.9		
Mine 3 Youngquist Sand				
Avg	8.12	6,530	Not tested	45
St Dev	0.07	2,060		14
% RSD	0.87	31.6		30
% RE	2.22	85.1		80
Mine 4 Calhoun Sand				
Avg	4.48	72,300	Not tested	Not tested
St Dev	0.28	35,000		
% RSD	6.24	48.4		
% RE	14.1	107		
Mine 5 Angelo’s Sand				
Avg	4.64	17,500	Not tested	31
St Dev	0.21	2,550		22
% RSD	4.49	14.6		71
% RE	15.7	40.0		194
Mine 6 Sebring Sand				
Avg	4.38	35,300	Not tested	8
St Dev	0.09	7,030		2
% RSD	1.98	19.9		30
% RE	8.4	58.1		80
Mine 7 Clermont Sand				
Avg	7.40	22,700	Not tested	Not tested
St Dev	0.27	3,260		
% RSD	3.72	14.4		
% RE	11.6	35.3		
Mine 8 Alico Road Sand				
Avg	8.51	9,940	Not tested	Not tested
St Dev	0.37	1,510		
% RSD	4.31	15.1		
% RE	11.4	47.8		

8.3.2 FM for pH

In the ruggedness study for pH, factors such as transport temperature, storage temperature, soil moisture content, sample mass, equilibration techniques, electrode differences, and salt addition were varied (Appendix A). Factor perturbations were tried on a minimum of two soils. For sands from mines 5 through 8, each ruggedness study for pH was repeated, thus expanding the total number of pH determinations from 8 to 16 and improving the sensitivity of the ruggedness study with regard to factor effects (ASTM C1067). Except where amended with calcium chloride, pH samples from mines 5 through 8 were amended with 0.1 g potassium chloride per 100 mL or 100 g of sample.

Recall that for Santa Fe River sand tested during laboratory visits the %RSD and %RE for pH were 10.1% and 32.4%, respectively (Chapter 6, Section 6.4.1, Table 6-1) compared with the ruggedness study results shown in Table 8-11, which ranged from 0.87% to 6.24% (average 3.54%) and from 2.22% to 15.7% (average 10.3%) for the same statistics, respectively. None of the ruggedness studies for pH across all four sands mimicked the variability seen in the laboratory visits, which was likely dominated by electrode failure.

From the pH ruggedness study results for eight sands (Appendix A), no significant differences were detected in pH averages for samples that were

- Transported in a cooler (10-20°C) versus at ambient temperatures (~30°C);
- Either 100-mL versus 100-g or 100-mL versus 30-g, except for Alico Road sand;
- Stirred briefly at 10-min intervals over a 30-min versus a 60-min period, if stirred or not stirred immediately before testing, if stirred vigorously or gently, or if stirred briefly at 10-min intervals over 30 min versus stirred once then allowed to sit for 30 min; and
- Tested with different electrodes, where each electrode was the same model 3-in-1 combination double-junction electrode but had a slightly different calibration slope and offset, or in the case Youngquist sand between two refillable glass bulb electrodes, both with temperature compensation, with differences in slopes and offset of 0.2% and 2.8 mV.

No significant differences were found in the standard deviations of all factors for Alico Road, Calhoun, Clermont, Jahna, and Youngquist sands.

Significant differences were found in the standard deviations of all factors for Angelo’s sand and Sebring sand (one replicate) (Appendix A, A-22, A-24, A-31) and these results may be due to one or more outlier pH values in the datasets, for example, determination 3 in Table A-21 (Appendix A). What these two soils have in common is that they were tested with the same model but different serial number electrodes, and each electrode had its own calibration. One explanation is that in switching back and forth between electrodes, at some point the right calibration was used with the wrong electrode. Another explanation is inadvertent carry-over of pH 5 buffer into the sample. The consequence of these outliers was to dull the sensitivity of the study to factor effects; this consequence was mitigated, however, because the experiments were duplicated.

A significant difference was detected in pH average but not standard deviation in Calhoun sand with and without the addition of 0.1 g of potassium chloride as an ionic strength adjustment (Appendix A, A-18). No significant difference was detected in pH average or standard deviation in Jahna sand with and without the addition of 0.1 g of potassium chloride

A significant difference was detected in pH average but not standard deviation in Wimauma sand when comparing two different electrodes (Appendix A, Table A-2). Both electrodes had glass bulbs but one was refillable and temperature-compensated and the other was disposable and without temperature compensation; between the electrodes the differences in slope and offset were at least 1.7% and 6.5 mV, respectively.

For Alico Road and Clermont sands, samples amended with calcium chloride had significantly lower pH averages than those samples amended with potassium chloride (Appendix A, Tables A-40, A-42, A-43, A-50). For Alico Road sand, this effect was seen only with 16 rather than 8 determinations.

For Alico Road, Clermont, and Sebring sands, storage temperature had a significant effect on average pH, with a higher pH for cold storage of Alico Road and Sebring sands and a higher pH for warm storage of Clermont sand (Appendix A, Tables A-33, A-34, A-43, A-50). For Alico Road and Sebring sand, storage temperature effects were seen only with 16 rather than 8 determinations.

In summary, these results suggested that the FM for pH was most sensitive to the electrode condition, to the ionic strength of the soil solution, to the choice of salt, if salt is used to increase the ionic strength, and to storage temperature. The impact of these factors on pH is discussed further in Chapter 9, Section 9.2.

8.3.3 FM for minimum resistivity

In the ruggedness study for resistivity, factors considered included transport temperature, storage temperature, “as-received” versus dried samples, sample mass, soil box size, increments of water addition, dilution water conductivity, equilibration period, rinsing and topping off the box with sample, and the amount of water of sample transferred to the box (Appendix A). Factor perturbations were tried on a minimum of two soils.

Recall that from the laboratory visits (Chapter 6, Section 6.4.2, Table 6-3) for Santa Fe River sand the %RSD and %RE for minimum resistivity were 11.9% and 41.7%, respectively, compared with the ruggedness study ranges of 13.1% to 48.4% (average 21.5%) and 35.5% to

107% (average 57.0%) for the same statistics, respectively (Table 8-11). The ruggedness studies for minimum resistivity across all four sands mimicked the variability seen in laboratory visits and revealed an additional source of variability.

No significant differences were detected in either minimum resistivity averages or standard deviations for samples that were

- Transported in a cooler (~10 - 20°C) versus at ambient temperatures (~30°C);
- Stored in a refrigerator (~4°C) or at room temperature (~23°C);
- Tested "as-received" or when air-dried and sieved;
- Not equilibrated or equilibrated overnight with 10% dilution water;
- Not equilibrated or equilibrated for 30 min with 20% dilution water;
- Placed in a soil box that was rinsed or not rinsed with dilution water between tests, or placed at or just below the rim of the soil box;
- Either 1.0-kg or 0.5- kg samples or 1.0-kg and 1.5-kg samples;
- Altered in wiring with the P1 and C1 and P2 and C2 terminals on the resistivity meter shorted; and
- Tested with water added in increments of either 100 mL or 50 mL.

Significantly lower minimum resistivity averages but not standard deviations were detected in Calhoun and Youngquist sands when the soil slurry created by sequential water additions was decanted to the soil box as mostly soil or as mostly water for studies (Appendix A, Tables A-14, A-20). This effect was explored further in a factor analysis study and is discussed in Chapter 9 (Section 9.2).

A significantly higher standard deviation of minimum resistivity was detected in Angelo's sand (Appendix A, Table A-27) for testing with dilution water of >1,000,000 ohm-cm versus with dilution water amended with sodium chloride such that the resistivity was 175,000 ohm-cm.

Significantly higher minimum resistivity averages were seen for Alico Road and Clermont sands (Appendix A, Tables A-45, A-52) when these sands were tested with large soil box versus a small soil box. A significantly higher standard deviation was seen in Clermont sand (Appendix A, Table A-45) for tests using a small soil box but for Angelo's sand (Appendix A, Table A-27) these results were reversed. Both soil boxes were manufactured by McMiller and had an area-to-length ratio of 1 cm; the capacities were 80 mL and 270 mL for the small and large box, respectively.

In summary, these results suggested that the FM for minimum resistivity was most sensitive to the amount of water included in soil slurry during the test procedure, to the size of the soil box, and to the resistivity of the dilution water. The impact of these factors on minimum resistivity is further explored in Chapter 9 (Section 9.2).

8.3.4 FM for sulfate

In the ruggedness study for sulfate, factors considered included transport temperature, storage temperature, drying temperature, acid addition, extraction and filtration techniques, changes in the calibration curve, and the use of blanks and sulfate spikes (Appendix A).

Recall that from the laboratory visits (Chapter 6, Section 6.4.4, Table 6-7) for a 30-ppm aqueous sulfate standard the %RSD and %RE for sulfate were 34.1% and 146%, respectively, compared with the ruggedness study ranges of 30% to 70% (average 46.5%) and 80% to 194% (average 129%) for the same statistics, respectively (Table 8-11). The ruggedness studies for sulfate across both sands mimicked the variability seen in the laboratory visits and revealed an additional source of variability. For Wimauma and Youngquist sands, all sample extracts were filtered through a 0.45-μm membrane prior to analysis for sulfate.

For Wimauma and Youngquist sands, no significant differences were detected in either minimum resistivity averages or standard deviations for samples that were

- Transported in a cooler (~10-20°C) and stored in a refrigerator (~4°C) versus transported at ambient temperatures (~30°C) and stored at room temperature (~23°C);
- Extracted with a 3:1 water-to-soil ratio versus a 1:1 water-to-soil ratio followed by post-filtration dilution by a factor of three; and
- Filtered through a fast, coarse paper or centrifuged to remove suspended particles.
- Not spiked or spiked with a 20 ppm sulfate standard. Adding a spike can increase the total sulfate concentration to a concentration above the method detection level; the concentration of the spike is then subtracted from the total concentration to get the sample sulfate concentration.
- Zeroed with a reagent blank versus an unreacted sample for a blank. The purpose of the unreacted sample blank is to zero out any remaining color or suspended particles; that no differences were measured between these blanks means that steps taken to clarify the sample were successful.

A significant difference was detected in sulfate concentration average but not standard deviation in Youngquist sand (Appendix A, Table A-16) for samples tested on either Range 1 or Range 2 using the manufacturer's default sulfate calibration curve: Range 2 results were higher.

A significantly lower standard deviation but not average in sulfate concentration was detected in Wimauma sand (Appendix A, Table A-6) for samples dried either at 60°C or at 110°C.

For Angelo's and Sebring sands, no significant differences were detected in sulfate concentration averages and standard deviations for samples that were

- Transported in a cooler (~10-20°C) and stored in a refrigerator (~4°C) versus transported at ambient temperatures (~30°C) and stored at room temperature (~23°C);
- Dried at 60°C versus 110°C;
- Amended with or without a few drops of acid added to help settle suspended particles in the soil extract;
- Filtered with a 0.45-micron membrane or not filtered after filtration with a coarse, fast filter; and
- Not spiked or spiked with a 20-ppm sulfate standard.

Significant differences in both sulfate concentration average and standard deviation were seen for Sebring sand (Appendix A, Table A-38) tested with different lot numbers. A significantly higher standard deviation was seen for Angelo's sand (Appendix A, Table A-29) when tested with the photometer calibration curve on Range 2 versus Range 1.

In summary, these results suggested that the FM for sulfate was sensitive to the sulfate calibration curve, reagent lot number, and possibly to the drying temperature. The impact of these factors on sulfate concentration is further explored in Chapter 9 (Sections 9.1 and 9.2).

8.4 Summary

In summary, ruggedness study results suggested that factors important to method bias and precision were for

- FM for pH: soil ionic strength, equilibration period, electrode condition, choice of salt if amended with salt, and storage temperature;
- FM for minimum resistivity: amount of water versus soil decanted into the soil box during the test procedure, volume of soil box, and resistivity of dilution water;

- FM for chloride: soil mass; and
- FM for sulfate: sulfate calibration curve, reagent lot number, and possibly drying temperature.

For the FM for chloride, also noted were issues with the digital titrator that makes it unsuitable for a standard test method.

9 Treatment and Other Studies

9.1 <u>Treatment Studies</u>

Treatment studies were conducted to assess the impact of transport, storage, and processing of backfill samples on sample pH, minimum resistivity, chloride, and sulfate levels. Backfill samples from mines 1 through 4 were tested with the current versions and mines 5 through 8 with proposed revised versions of the FMs. Refer to Chapter 11, Section 11.2.3, for a summary of changes between these versions.

9.1.1 Summary statistics

In Table 9-1 were presented for each method and soil the average, standard deviation, %RSD, and %RE across all treatments. These averages were included for USF in Chapter 7, Section 7.4, Table 7-2. Refer to Appendix B for treatment details, method calibration data, and results. For pH and minimum resistivity, three treatments were investigated: treatment 1 (on-site), on-site analysis immediately after sampling; treatment 2 (ambient), transport under ambient conditions (~30°C), storage at room temperature (~23°C), and testing at "as-received" soil moisture content; and treatment 3 (cold), transport in a cooler on ice (~20°C), storage in a refrigerator (~4°C), and testing at "as-received" soil moisture content. For some but not all soils, additional treatments were investigated such "as-received" versus air-dried soils, or for soils dried at different temperatures, as examples. For sulfate and chloride the primary interest was in whether the drying temperature, either 60°C or 110°C, affected measured concentrations.

Table 9-1 Summary Statistics for Treatment Study Results

Statistic	pH	Minimum Resistivity, ohm-cm	Soil Chloride Concentration, ppm	Soil Sulfate Concentration, ppm
Mine 1 Wimauma				
Avg	4.65	44,700	Below detection	10
St Dev	0.11	3,010		2
%RSD	2.26	6.74		16
%RE	9.67	24.6		30
Mine 2 Jahna				
Avg	5.16	116,000	Below detection	Below detection
St Dev	0.17	8,210		
%RSD	3.21	7.09		
%RE	11.8	25.9		
Mine 3 Youngquist				
Avg	8.23	9,150	Below detection	36
St Dev	0.12	975		6
%RSD	1.42	10.7		16
%RE	4.74	35.5		50
Mine 4 Calhoun				
Avg	4.58	104,000	Below detection	Below detection
St Dev	0.08	12,000		
%RSD	1.78	11.5		
% RE	5.90	38.4		
Mine 5 Angelo’s Sand				
Avg	4.59	17,830	Below detection	24
St Dev	0.03	1030		4
% RSD	0.76	5.78		17
% RE	3.27	14.0		62
Mine 6 Sebring Sand				
Avg	4.38	36,060	Below detection	16
St Dev	0.06	3750		5
% RSD	1.38	10.4		33
%RE	4.57	26.4		75
Mine 7 Clermont Sand				
Avg	7.54	28,170	Below detection	Below detection
St Dev	0.17	3650		
%RSD	2.23	13.0		
%RE	8.62	32.0		
Mine 8 Alico Road				
Avg	8.99	11,170	Below detection	Below Detection
St Dev	0.05	430		
%RSD	0.58	3.88		
%RE	2.00	13.4		

9.1.2 FM for pH

For all mines, on-site pH measurements were made in triplicate, took ~one hr, and required at a minimum a portable pH meter (AP85/13-62-AP55, with ATC), a flat surface, 2 L of dilution water, and beakers, buffers, stirring rod, tissues, rinse bottle, and a 100-mL scoop. The portable pH meter gave erratic readings during two site visits when the mid-morning temperature quickly reached 30 ^{o}C, but readings stabilized once the instrument was cooled by shade.

9.1.2.1 Mines 1 through 4

For samples from mines 1 through 4, three treatments were investigated: treatment 1 (on-site), on-site analysis with 1 hr after sampling; treatment 2 (ambient), transport under ambient conditions (~30°C), storage at room temperature (~23°C), selection by quartering, and testing at "as-received" soil moisture content; and treatment 3 (cold), transport in a cooler on ice (~20°C), storage in a refrigerator (~4°C), selection by quartering, and testing at "as-received" soil moisture content. An additional treatment (air-dried) was investigated for mines 1 through 3: transport under ambient conditions (~30°C), storage at room temperature (~23°C), air-dried, sieved through a No. 10 (2 mm) mesh, and sample selection by mechanically splitting. Although the soil processing steps were varied between treatments, the analytical test protocol remained the same: 100 mL of soil were diluted with 100 mL of deionized water, stirred for ~20 s at 10-min intervals over 30 min, and tested with the same portable pH meter and compatible electrode (AP85/13-62-AP55). Soils that were stored cold were brought to room temperature before testing.

The pH repeatability across all treatments was the best for Youngquist sand with an average, standard deviation, %RSD, and %RE of 8.23, 0.12, 1.42%, and 4.74%, respectively, and worst for Jahna sand with an average, standard deviation, %RSD, and %RE of 5.16 pH units, 0.17 pH units, 3.21%, and 11.8%, respectively (Table 9-1). Refer to Appendix B for the treatment details, method calibration data, and results. Treatment study results for pH are summarized below.

- For Wimauma, Jahna, and Calhoun, no significant differences were detected in pH averages or standard deviations between on-site, ambient, and cold treatments.

- For Jahna sand, the average pH was significantly higher for air-dried treatment than for ambient treatment; for Wimauma sand, pH was significantly higher for air-dried than for on-site or ambient treatments. No significant differences were detected in pH standard deviations.

- For Youngquist sand, average pH was significantly higher for cold treatment than for on-site or ambient treatment; no significant differences were detected in pH standard deviations.

- For Youngquist sand, average pH was significantly lower in air-dried sand than for ambient or cold treatments. No significant differences were detected in pH standard deviations.

These results suggested that the FM for pH may be sensitive to air-dried versus "as-received" samples and possibly to samples transported and stored at cold versus at ambient temperatures.

9.1.2.2 Mines 5 through 8

For samples from mines 5 through 8, four treatments were investigated: treatment 1 (on-site), on-site analysis within 1 hr after sampling; treatment 2 (ambient), transport under ambient conditions (~30°C), storage at room temperature (~23°C), and testing at "as-received" soil moisture content; treatment 3 (cold), transport in a cooler on ice (~10 - 20°C), storage in a refrigerator (~4°C), and testing at "as-received" soil moisture content, and 4 (air dried) transport under ambient conditions, storage at room temperature, dry at 60°C, and sieved through a No. 10 mesh. Although the soil processing steps were varied between treatments the analytical test protocol remained the same: 100 g of soil were amended with 0.1 g potassium chloride, diluted with 100 mL of deionized water, and stirred for ~20 s at 10-min intervals over 30 min. In the field, the samples were tested with a portable pH meter and compatible electrode (AP85/13-620-AP55); in the laboratory, however, samples were tested with a benchtop meter (AB150/13-620-631) as well as with the portable meter to compare the two instruments. Soils that were stored cold were brought to room temperature before testing. Refer to Appendix B for the treatment details, method calibration data, and results.

For Angelo's sand, the average pH was significantly lower in dry soil for a benchtop meter versus a portable meter, a likely consequence of differences in meter/electrode calibrations and low standard deviations for both measurements.

For Sebring sand, average pH measurements were significantly higher for cold versus warm measurements, consistent with ruggedness study results for the same soil (Chapter 8, Section 8.3.2).

For Clermont sand, there was a factor of 10 jump in pH standard deviations between on-site and laboratory measurements. The lowest pH average occurred for sand transported and stored cold, as compared with on-site measurements, consistent with results for a ruggedness study (Chapter 8, Section 8.3.2). In contradiction, the average pH measurement by portable pH meter of samples transported and stored cold was higher than averages for all other treatments and significantly higher than for cold and dry pH measurements made with a benchtop meter.

For Alico Road sand, dried and sieved soil had a significantly lower pH than for ambient treatments as tested with both the portable and benchtop pH meters, which can be explained by the removal of a significant fraction of particle mass in the sieving process. Of the 10 soils tested in this project, Alico Road was the only soil that tested positive for the presence of carbonates (a few drops of 10% hydrochloric acid on ~1 gram of sample). The fraction retained on the No. 10 sieve was rich in carbonates and its removal diminished the observed pH. Refer to Section 9.2.10 for further discussion. For this soil, sieving shifted the pH from not acceptable to acceptable based on FDOT's criterion that select backfill have a pH ≤ 9.0. This finding offers a compelling argument to test pH samples "as received."

If the soil pH were sensitive to transport and/or storage temperature, under what conditions do the laboratory measurements best duplicate on-site measurements? The square root of the sum of squares for the differences between pH averages for on-site versus warm, cold, and dry soil treatments yielded 0.22, 0.07, and 0.14 pH units, respectively; thus the least error was seen between soil on-site pH averages and pH averages for soil that had been transported cool and stored cold.

The pH repeatability across all treatments was the best for Alico Road sand with an average, standard deviation, %RSD, and %RE of 8.99, 0.05, 0.58%, and 2.00%, respectively, and for worst for Clermont sand with an average, standard deviation, %RSD, and %RE of 7.54, 0.17, 2.23%, and 8.62%, respectively (Table 9-1). In summary, for one soil the average pH measurement was significantly lower after the soil was dried and sieved than for other treatments, a likely consequence of carbonate minerals retained on the sieve. For one soil, the average pH measurement was significantly lower for warm transport and storage than for cool transport and cold storage; across all four soils the average pH observations were in reasonable agreement between measurements made on-site and those made in the laboratory for soils transported cool and stored cold.

9.1.3 FM for minimum resistivity

On-site minimum resistivity measurements were made in triplicate, took ~two hr, and required a portable resistivity meter with leads, a flat surface, 2 L of dilution water, soil box, large bowl, spatula, and spoon. The resistivity meter did not have a temperature compensation feature.

9.1.3.1 Mines 1 through 4

For samples from mines 1 through 4, four treatments were investigated: treatment 1 (on-site), on-site analysis within two hr after sampling; treatment 2 (ambient), transport under ambient conditions (~30°C), storage at room temperature (~23°C), selection by quartering, and testing at "as-received" soil moisture content, and treatment 3 (cold), transport in a cooler on ice (~20°C), storage in a refrigerator (~4°C), selection by quartering, and testing at "as-received" soil moisture content; a fourth treatment (air-dried) was transport under ambient conditions (~30°C), storage at room temperature (~23°C), air-dried or dried at 60°C, sieved through a No. 10 (2 mm) mesh, and sample selection by mechanically splitting. Although the soil processing steps were varied between treatments, the analytical test protocol remained the same: use of a Nilsson Model 400 resistivity meter and leads, a large soil box, 1,000 g of soil, 100-mL increments of added deionized water, and soil-rich slurry content in the soil box. Refer to Appendix B for the treatment details, method calibration data, and results. Treatment study results for minimum resistivity are summarized below.

- For Wimauma sand, minimum resistivity averages were higher for air-dried sand than for on-site or cold treatments; no significant differences were detected in minimum resistivity standard deviations.

- For Jahna sand, minimum resistivity averages were significantly lower for on-site treatment than for ambient and cold treatments and significantly higher for ambient treatment than for cold treatment or for air-dried sand. All three minimum resistivity measurements for cold treatment were the same, so the standard deviation was zero and significantly lower than for all other treatments.

- For Youngquist sand, on-site measurements were made with the resistivity meter terminals shorted, P1 to C1 and P2 to C2, which yielded resistivity readings that were ~15% higher than when terminals were not shorted. No significant difference was detected between the minimum resistivity average and standard deviation for on-site and warm treatments when both treatments had the terminals shorted. Minimum resistivity averages were significantly lower for cold treatment compared to warm treatment and for cold treatment compared to air-dried sand, where terminals were in their normal configuration (not shorted). Minimum resistivity standard deviation was significantly lower for air-dried sand than for on-site, warm, or cold treatments.

- For Calhoun sand, minimum resistivity averages were significantly lower for on-site treatment than for ambient and cold treatments, and significantly lower for air-dried sand than for ambient and cold treatment; minimum resistivity standard deviations were significantly lower for ambient treatment than for on-site and cold treatments.

The minimum resistivity repeatability across all treatments was the best for Wimauma sand with an average, standard deviation, %RSD, and %RE of 44,700 ohm-cm, 3,010 ohm-cm, 6.74%, and 24.6%, respectively, and the worst for Calhoun sand with an average, standard deviation, %RSD, and %RE of 104,000 ohm-cm, 12,000 ohm-cm, 11.5%, and 38.4%, respectively. These results suggested that the FM for resistivity may be sensitive to on-site analysis of soil samples. For the four sands tested, temperatures were 5 to 10°C higher for on-site analyses than for laboratory analyses; Equation 3-4 (Chapter 3, Section 3.3.1) predicted a 10% and a 17% decrease in resistivity between 23°C and 28°C and between 23°C and 33°C, respectively, and predicted fairly well the average difference in minimum resistivity between on-site and ambient treatments for all four sands. No consistent pattern was seen where minimum resistivity was significantly different between treatments other than on-site treatment.

The FM for resistivity was less compatible with field work, as the time, volume, and surface area requirements were greater than for pH. Moreover, the method was sensitive to temperature (Chapter 3, Section 3.3.1). An alternative approach to field measurement of resistivity is to measure conductivity using portable conductivity meter with automatic temperature compensation, as the inverse of conductivity is resistivity. The typical protocol for conductivity measurements, however, dilutes the sample well beyond that of the soil box measurements. Thus, field measurements of conductivity could serve as a screening tool but would not replace the FM for resistivity.

9.1.3.2 Mines 5 through 8

For samples from mines 5 through 8, three treatments were investigated: treatment 1 (ambient), transport under ambient conditions (~30°C), storage at room temperature (~23°C), and testing at "as-received" soil moisture content; treatment 2 (cold), transport in a cooler on ice (~10 - 20°C), storage in a refrigerator (~4°C), and testing at "as-received" soil moisture content; and treatment 3 (air dried), transport under ambient conditions, stored at room temperature, dried at 60°C, and sieved through a No. 10 mesh. Soils were brought to room temperature before testing. Although the soil processing steps were varied between treatments, the analytical test protocol remained the same: use of a Nilsson Model 400 resistivity meter and leads, a large soil box, 1,000 g of soil, 100-mL increments of deionized water, and water-rich slurry content in the soil box. Refer to Appendix B for treatment details, method calibration data, and results.

Treatment study results for minimum resistivity are summarized below.

- For Alico Road and Angelo's sands, the minimum resistivity average was significantly higher for cold treatment than for warm or dry treatments,
- For Clermont sand, the minimum resistivity average was significantly lower for cold treatment than for warm or dry treatment, and
- For Sebring sand, the minimum resistivity average was significantly higher for dry treatment than for warm or cold treatments.

The minimum resistivity repeatability across all treatments was the best for Alico Road sand with an average, standard, %RSD, and %RE of 11,190, 430, 3.88% and 13.8%, and the worst for Clermont sand with an average, standard deviation, %RSD, and %RE of 28,170 ohm-cm, 3,650 ohm-cm, 13.0%, and 32.0%, respectively. Standard deviations were low or zero, for the most part, which made it easier to diagnose differences between treatment means. Temperature did not appear to be a contributing factor in the differences between treatment means. These results suggested that variability in sample minimum resistivity between laboratories could be reduced if laboratories processed samples in a similar manner, for example, with transport under ambient conditions and samples stored at room temperature.

For pH measurements in sieved soils, the pH changed for soils with a significant mass retained on the sieve; by inference in some soils under similar circumstances the minimum resistivity could change. AASHTO T288 requires the soil be sieved for a minimum resistivity measurement but provides guidance for separating and testing the fraction retained on a No. 10 sieve. Testing soils "as received" was recommended.

9.1.4 FM for chloride

For chloride the primary objectives were to find the best technique for producing a clear sample and to determine if drying temperature, either 60°C or 110°C, affected measured concentrations. Although the soil processing steps were varied between treatments, the analytical test protocol remained the same. A Hach Chloride Low Range Test Kit Model 8-P was used. A 23-mL sample of filtered (clear) soil extract was amended with one packet of Chloride 2 reagent (potassium dichromate and sodium bicarbonate) and titrated to a reddish color with 0.0493 N silver nitrate using a calibrated dropper. A blank and a check standard were titrated along with the sample. The number of drops (always one drop) required to titrate the blank was subtracted from the number of drops required to titrate the sample and check standard. The blank-corrected number of drops was then multiplied by 5 ppm per drop and by the dilution factors, which were three for the soil extract and one for the check standard. Refer to Appendix B for the treatment details, method calibration data, and results.

Wimauma sand was transported in a cooler on ice (~20°C), stored in a refrigerator (~4°C), selected by quartering, dried at either 60°C or 110°C, and sieved through a No. 10 (2 mm) mesh. A soil extract was prepared by diluting 100 g of soil with 100 mL of water; this extract was shaken for 20 s allowed to settle for 1 hr, shaken again for 20 s, allowed to settle for 36 hr, filtered through a coarse, fast filter (Fisher Q-8), and finally diluted by a factor of three. The resulting extract was clear.

Jahna sand was transported under ambient conditions (~30°C), stored at room temperature (~23 °C), dried at either 60°C or 110°C, sieved through a No. 10 (2 mm) mesh, and selected by mechanical splitting. A soil extract was prepared by diluting 100 g of soil with 100 mL of water; this extract was shaken for 20 s allowed to settle for 1 hr, shaken again for 20 s, allowed to settle for 24 hr, then diluted by a factor of three and filtered through a 0.45-micron mixed cellulose ester membrane filter. The resulting extract was clear.

Youngquist sand was transported under ambient conditions (~30°C), stored at room temperature (~23°C), dried at either 60°C or 110°C, sieved through a No. 10 (2 mm) mesh, and selected by mechanical splitting. A soil extract was prepared by diluting 300 g of soil with 100 mL of water; this extract was shaken for 20 s allowed to settle for 1 hr, shaken again for 20 s, allowed to settle for 24 hrs, then filtered first through a coarse, fast filter (Whatman 4), second through another coarse, fast filter (Fisher Q-8), and finally filtered through a 0.45-micron mixed cellulose ester membrane filter. The resulting extract was clear.

Calhoun sand was transported under ambient conditions (~30°C), stored at room temperature (~23°C), dried at either 60°C or 110°C, sieved through a No. 10 (2 mm) mesh, and selected by mechanical splitting. A soil extract was prepared by diluting 300 g of soil with 100 mL of water;

this extract was shaken for 20 s allowed to settle for 1 hr, shaken again for 20 s, allowed to settle for 24 hrs, then filtered through a coarse, fast filter (Fisher Q-8) and finally filtered through a 0.45-micron mixed cellulose ester membrane filter. The resulting extract was clear. For a third treatment, Calhoun sand was transported in a cooler on ice (~20°C), stored in a refrigerator (~4°C), dried 60°C or 110°C, sieved through a No. 10 (2 mm) mesh, and selected by mechanical splitting. The rest of the soil processing was the same as for the first two treatments.

Angelo's, Sebring, Clermont, and Alico Road sands were transported under ambient conditions (~30°C), stored at room temperature (~23°C), dried at either 60°C or 110°C, sieved through a No. 10 (2 mm) mesh, and selected by mechanical splitting. A soil extract was prepared by diluting 300 g of soil with 100 mL of water; this extract was shaken for 20 s allowed to settle for 1 hr, shaken again for 20 s, allowed to settle for 24 hr, then filtered through a coarse, fast filter (Fisher Q-8) and finally filtered through a 0.45-micron mixed cellulose ester membrane filter. The resulting extract was clear. For Clermont sand two additional treatments included testing of samples that were transported in a cooler on ice (~20°C), stored in a refrigerator (~4°C), dried 60°C or 110°C, sieved through a No. 10 (2 mm) mesh, and selected by mechanical splitting. The rest of the soil processing was the same as for the first two treatments.

Chloride concentrations in all eight sands were below the stated method detection level of 5 ppm (15 ppm if multiplied by a dilution factor of three to convert to a soil concentration). The Youngquist sand was the most difficult of the four sands to clarify. Although a clear sample was obtained with final filtration through a 0.45-micron membrane filter, the membrane filter was quickly clogged and filtering enough extract to test took ~30 min.

9.1.5 FM for sulfate

For sulfate the primary objectives were to find the best technique for producing a clear sample and to determine if drying temperature, either 60°C or 110°C, affected measured concentrations. The soil processing steps were varied between treatments, but the analytical test protocol remained the same. A Hach Photometer II Sulfate Test Kit was used. A 10-mL sample of filtered (clear) soil extract in a test cell was amended one packet of SulfaVer 4 reagent (barium chloride and citric acid), gently mixed, and allowed to sit for 5 min. A second 10-mL sample of filtered extract was handled in like manner but no reagent was added to it. The photometer was zeroed with an unamended sample and the sulfate concentration was read directly from the photometer with the amended sample. Samples were tested on the built-in photometer sulfate calibration curve labeled Range 1, except for Angelo's sand, which was tested on both Range 1 and Range 2. This reading was multiplied by the dilution factor to get the soil sulfate concentration. A blank of dilution water and a check standard were also prepared and tested. Treatments by soil were as described for chloride in the previous section. Refer to Appendix B for the treatment details, method calibration data, and results.

The sulfate repeatability across all treatments was the best for Wimauma sand with an average, standard deviation, %RSD, and %RE of 10 ppm, 2 ppm, 16%, and 30%, respectively, and worst for Sebring sand with an average, standard deviation, %RSD, and %RE of 16 ppm, 5 ppm, 33%, and 75%, respectively (Table 9-1). Sulfate concentrations were below the stated method detection of 2 mg/L (6 mg/L when multiplied by a dilution factor of three to get the soil concentration) for Jahna, Calhoun, Clermont, and Alico Road sands.

- For Wimauma, Youngquist, and Angelo's sands, no significant differences were detected in sulfate averages or standard deviations where treatments varied only by the drying temperature, which was either 60°C or 110°C.

- For Angelo's sand, the average sulfate concentration was higher with sulfate calibration curve Range 2 when compared with Range 1.

- For Sebring sand, the average and standard deviation sulfate concentration was significantly higher for sand dried at 110°C versus 60°C.

The results for Sebring sand suggested that for some soils, the FM for sulfate is sensitive to drying temperature. Since the moisture content is higher after drying at 60°C rather than 110°C, a 100-g aliquot would contain less soil and thus less sulfate. That said, drying soil at a higher temperature can cause gypsum present in some soils to lose its waters of hydration and to shift to a more water-soluble mineral phase, thus increasing the observed sulfate concentration (Herrero et al., 2009). The current FM allows drying the soil either at room temperature or at 110°C. To reduce variability in sulfate concentrations measured between laboratories, amending the FM to allow drying the soil from room temperature up to 60°C, consistent with the AASHTO T290 drying temperature, was recommended.

9.2 Other Factor Analysis Studies

9.2.1 Effect of ionic strength and pH electrode on pH measurement

To look further into the fixed effects on pH of ionic strength and electrode condition, a replicated factor analysis experiment was conducted with two unmodified soils, Starvation Hill and Santa Fe River, where each soil was diluted with and without 0.01 M calcium chloride ($CaCl_2$), and each dilution was tested with both pH electrode 1 and electrode 2. Both pH electrodes were Accumet, with part numbers 2242017P and 8074017P for electrode 1 and electrode 2, respectively. Offset voltages for calibration with pH 7 and pH 10 buffers were 1.8 mV for electrode 1 and 25.4 mV for electrode 2.

Results showed that dilution of Starvation Hill and Santa Fe River soils with 0.01 M calcium chloride shifted the average pH lower by 0.58 pH units, compared to a shift in average pH between soils of 0.17 pH units and between electrodes of 0.14 pH units, where electrode 2 had a higher pH (Figure 9-1, Table 9-2). Analysis of variance (ANOVA) showed that it was unlikely that the average pH between soils, between electrodes, and between calcium chloride treatments were equal (Table 9-3). Interactions were not significant, with the possible exception of the interaction between pH electrode and amendment (Table 9-3), where the difference in average pH was greater for calcium chloride-amended soils when pH was measured with electrode 2.

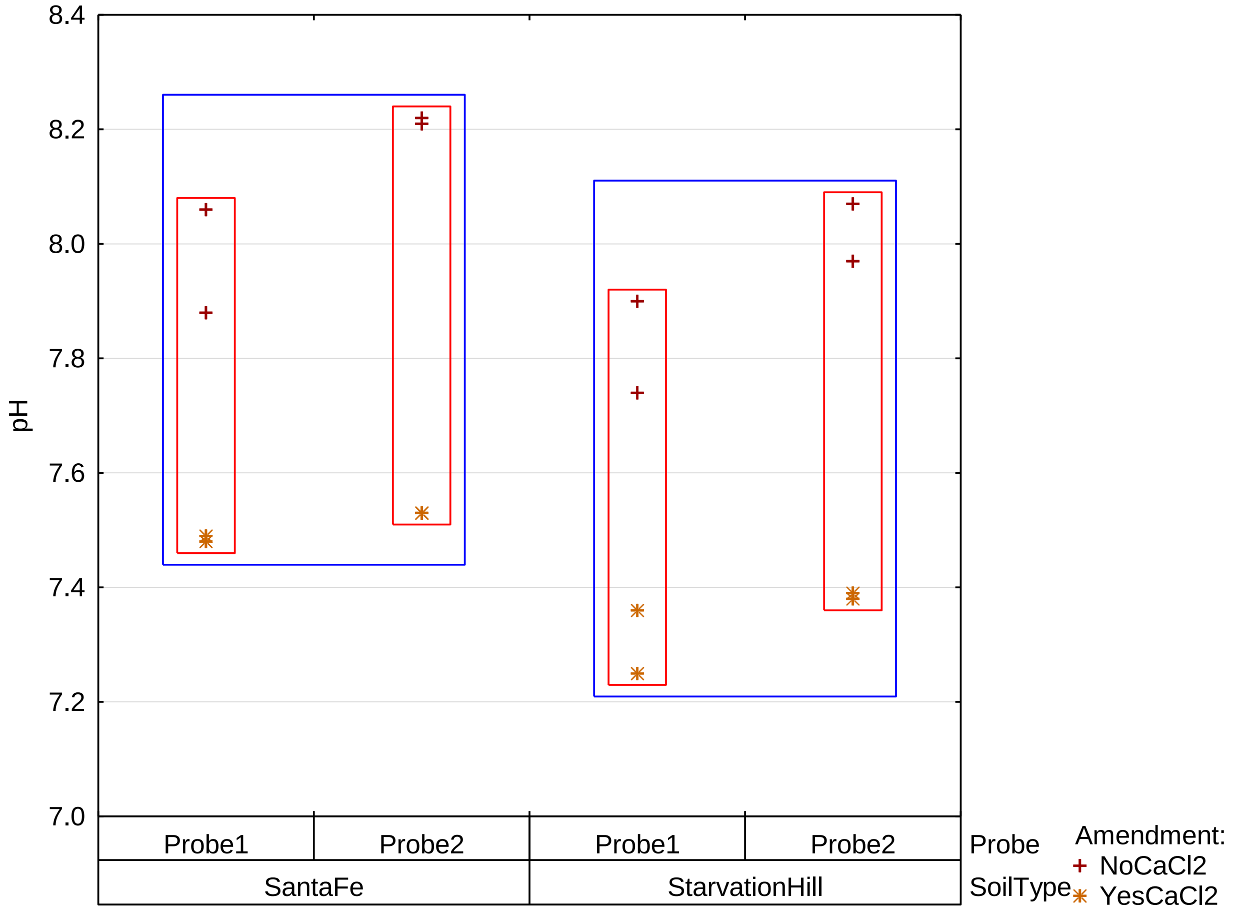


Figure 9-1. Variability plot of pH by soil type, pH electrode, and $CaCl_2$ amendment.

Table 9-2 Comparison of pH Means by Soil Type, pH Electrode, and Calcium Chloride Amendment

Effect	Descriptive Statistics (Statistica pH Spreadsheet)			
	Level of Factor	Number of Samples	pH Mean	pH Std Dev
Total		16	7.72	0.33
Soil Type	Santa Fe	8	7.80	0.33
Soil Type	Starvation Hill	8	7.63	0.32
Electrode	Electrode 1	8	7.65	0.29
Electrode	Electrode 2	8	7.79	0.37
Amendment	No $CaCl_2$	8	8.01	0.17
Amendment	Yes $CaCl_2$	8	7.43	0.10

Table 9-3 ANOVA for pH by Soil Type, pH Electrode, and $CaCl_2$ Amendment

	Fixed Effect Test for pH (Statistica pH Spreadsheet) Restricted Maximum Likelihood (REML) Type V decomposition			
Effect	Num. DF	Den. DF	*F*	*p*
Soil Type	1	8	22.3	0.001
Electrode	1	8	16.2	0.004
Amendment	1	8	268	0.000
Soil Type*Electrode	1	8	0.005	0.946
Soil Type*Amendment	1	8	0.0199	0.891
Electrode*Amendment	1	8	5.10	0.054
Soil Type*Electrode*Amendment	1	8	0.318	0.588

To summarize, if the ionic strength of the soil solution were low, adding a small amount of salt to the sample to increase its ionic strength could reduce the sensitivity of the pH measurements to minor variations in technique. In such a case, however, the measured pH may shift lower by more than 0.5 pH units, and the condition of the pH electrode may have a greater impact on the measured pH.

9.2.2 Effect of incremental water volume and pre-wetting on minimum resistivity

To look further into the fixed effects on soil resistivity of incremental water volume and of pre-wetted versus dry soil, a replicated factor analysis experiment was conducted with two salt-amended soils: Starvation Hill and Santa Fe River, where for each a pre-wetted and dry soil sample was tested with the addition of either 75 mL or 100 mL of deionized water volume increments. The average soil resistivity was lowered by 156 ohm-cm with the addition of 75 mL instead of 100 mL of water volume increments and lowered by 106 ohm-cm when the soil was pre-wetted overnight prior to testing (Figure 9-2, Table 9-4). Analysis of variance (ANOVA) showed that the hypothesis that the average resistivity between soils, between incremental water volumes, and between pre-wetted versus dry soil were equal cannot be rejected (Table 9-5). Interactions were not significant (Table 9-5).

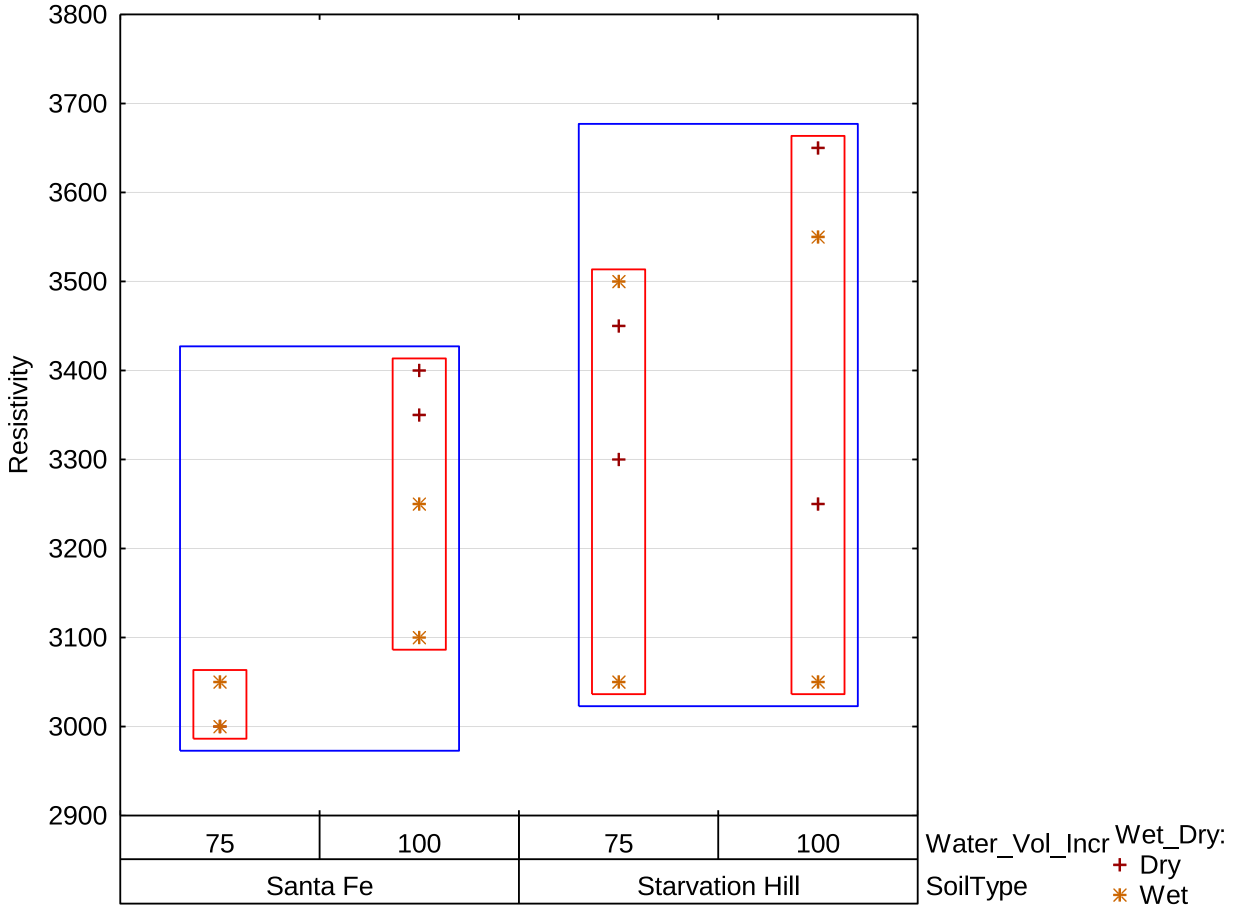


Figure 9-2. Variability plot of soil resistivity (ohm-cm) by soil type, incremental water volume (ml), and pre-wetted versus dry soil.

Table 9-4 Comparison of Soil Resistivity Means by Soil Type, Incremental Water Volume, and Pre-Wetted versus Dry Soil

Effect	Descriptive Statistics (Statistica Resistivity Spreadsheet)			
	Level of Factor	Number of Samples	Resistivity Mean (ohm-cm)	Resistivity Std Dev (ohm-cm)
Total		16	3,250	219
Soil Type	Santa Fe	8	3,140	166
Soil Type	Starvation Hill	8	3,350	225
Incr Water Vol	75	8	3,170	214
Incr Water Vol	100	8	3,330	207
Pre-Wetted vs Dry	Dry	8	3,300	220
Pre-Wetted vs Dry	Wet	8	3,190	218

Table 9-5 ANOVA for Soil Resistivity Means by Soil Type, Incremental Water Volume, and Pre-Wetted versus Dry Soil

Effect	Fixed Effect Test for Resistivity (Statistica Resistivity Spreadsheet) Restricted Maximum Likelihood (REML) Type V decomposition			
	Num. DF	Den. DF	*F*	*p*
Soil Type	1	8	4.11	0.077
Incremental Water Volume	1	8	2.36	0.163
Pre-Wetted vs Dry Soil	1	8	1.09	0.327
Soil Type*Incr Water Vol	1	8	1.09	0.327
Soil Type*Pre-Wetted vs Dry	1	8	0.034	0.858
Incr Water Vol*Pre-Wetted vs Dry	1	8	0.457	0.518
Soil Type*Incr Water Vol*Pre-Wetted vs Dry	1	8	0.185	0.679

To summarize, a change in incremental water volume did not significantly affect measured soil resistivity, so no change is recommended in the current practice of water volume increments of 100 mL. No significant difference was seen in soil resistivity between soil samples that were initially dry or pre-wetted overnight, so this additional method step is not recommended for soils that have been air-dried and sieved prior to testing.

9.2.3 Effects of extraction method and soil type on chloride measurements

To look further into the fixed effects of extraction method on chloride concentration, a replicated factor analysis experiment was conducted with two soils: Starvation Hill and Santa Fe River. Both soils were air-dried, sieved through a No. 10 sieve, and amended with 0.10 g/kg sodium chloride and 0.10 g/kg sodium sulfate. The first of two extraction methods was 100 g soil diluted with 100 mL of deionized water in a 500-mL flask, shaken for 20 s and allowed to settle for 1 hr then shaken again for 20 s, allowed to settle overnight, filtered by gravity through a coarse filter into a 500-mL flask and again allowed to settle overnight, and as a final step 50 mL of extract was decanted into a 250-mL flask and diluted to 150 mL. The second of two extraction methods was as described above, except that 100 g soil was diluted with 300 mL of deionized water and as a final step 150 mL of extract was decanted and filtered through a 47-mm diameter 0.45-micron membrane filter (Pall Metricel P/N 63069). Interestingly, the settling rate of soil particles was faster and the resulting extract clearer for a 1:1 (mass-to-volume) soil-to-water ratio. Both methods produced clear samples. The average chloride concentration was higher by 2 ppm and its standard deviation was lower by 5 ppm for the 1:1 soil-to-water extraction method (Extraction Method 1, Figure 9-3,Table 9-6) compared with membrane filtration (Extraction Method 2), although neither a *t*-test for means ($p = 0.65$) nor an *F*-test for variance ($p = 0.07$) were significant. Note that the variation in chloride concentrations for both revised extraction methods were lower than the variation reported in Table 5-2 (Chapter 5, Section 5.3) for salt-amended soil chloride concentration. Analysis of variance (ANOVA) showed that the hypothesis that the average chloride concentration between soils and extraction methods were equal cannot be rejected (Table 9-7). The interaction of soil type and extraction method was not significant (Table 9-7).

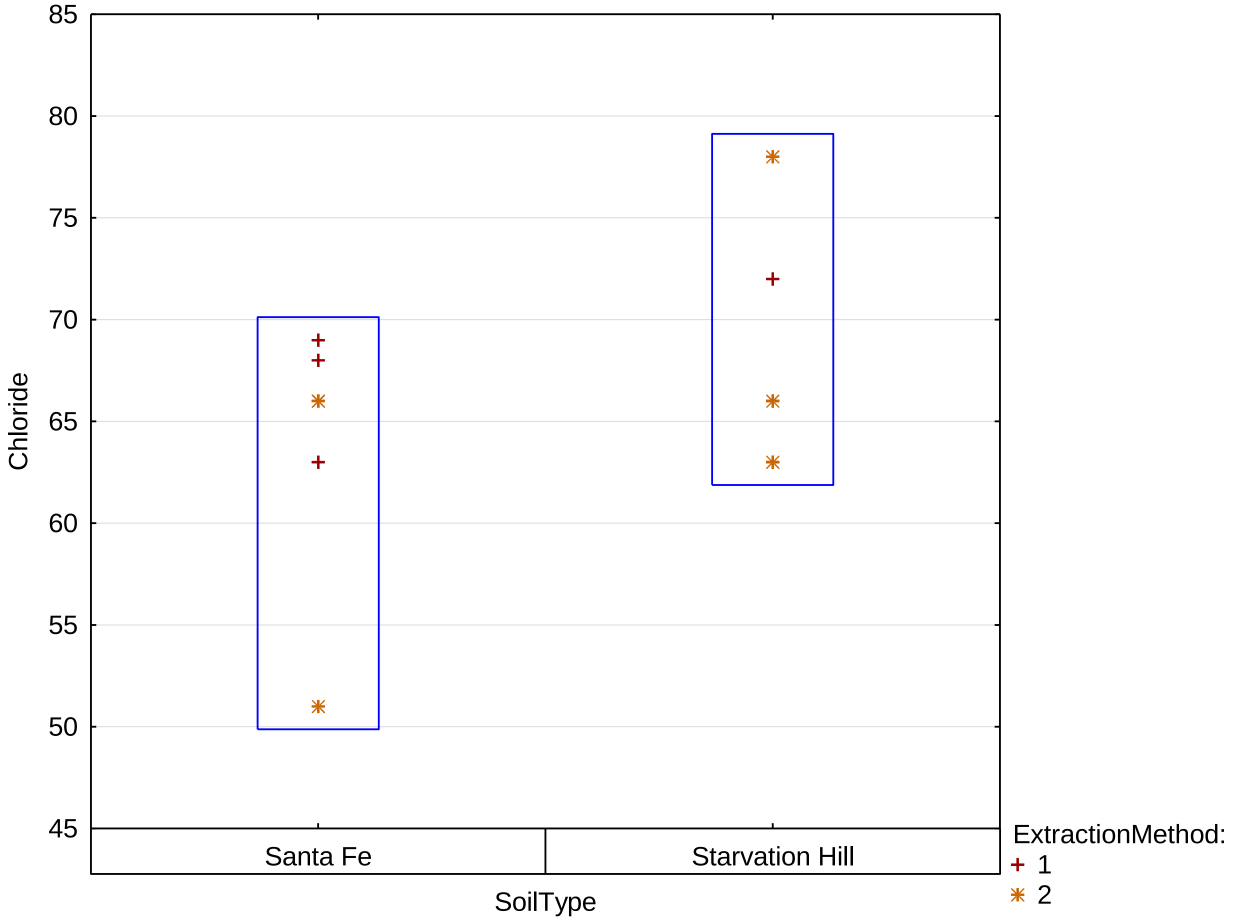


Figure 9-3. Variability plot of chloride concentration (ppm) by soil type and extraction method.

Table 9-6 Comparison of Soil Chloride Means by Soil Type and Extraction Method

Effect	Descriptive Statistics (Statistica Chloride Spreadsheet)			
	Level of Factor	Number of Samples	Chloride Mean (ppm)	Chloride Std Dev (ppm)
Total		12	65.9	6.36
Soil Type	Santa Fe	6	63.8	6.62
Soil Type	Starvation Hill	6	68.0	5.90
Extraction Method	1	6	66.8	3.54
Extraction Method	2	6	65.0	8.63

Table 9-7 ANOVA for Soil Chloride by Soil Type and Extraction Method

Effect	Fixed Effect Test for Chloride (Statistica Chloride Spreadsheet) Restricted Maximum Likelihood (REML) Type V decomposition			
	Num. DF	Den. DF	*F*	*p*
Soil Type	1	8	1.23	0.300
Extraction Method	1	8	0.238	0.639
Soil Type*Extraction Method	1	8	1.04	0.337

In summary, laboratory rather than field testing for chloride concentration in soil is recommended to accurately measure soil mass and to prepare a sample extract that is sufficiently clear of particles and color that may interfere with the chloride analysis. Both extraction methods produced clear sample extracts with no detectable difference in chloride concentration. Further testing of these two extraction methods on other soils is recommended.

9.2.4 Effect of extraction method on sulfate measurement

To look further into the fixed effects of extraction method on sulfate concentration, a replicated factor analysis experiment was conducted with two soils: Starvation Hill and Santa Fe River. Soils were prepared and extracted as described in the previous section for chloride. The average sulfate concentration was lower by 6 ppm and its standard deviation was lower by 4 ppm for the 1:1 soil-to-water extraction method (Extraction Method 1, Figure 9-4, Table 9-8) compared with membrane filtration (Extraction Method 2), although neither a *t*-test for means ($p = 0.29$) nor an *F*-test for variance ($p = 0.30$) were significant. Note that the variation in sulfate concentrations for both revised extraction methods spanned the variation reported in Table 5-2 (Chapter 5, Section 5.3) for salt-amended sulfate concentration. Analysis of variance (ANOVA) showed that the hypothesis that the average sulfate concentration between soils and extraction methods were equal cannot be rejected (Table 9-9). The interaction of soil type and extraction method was not significant (Table 9-9).

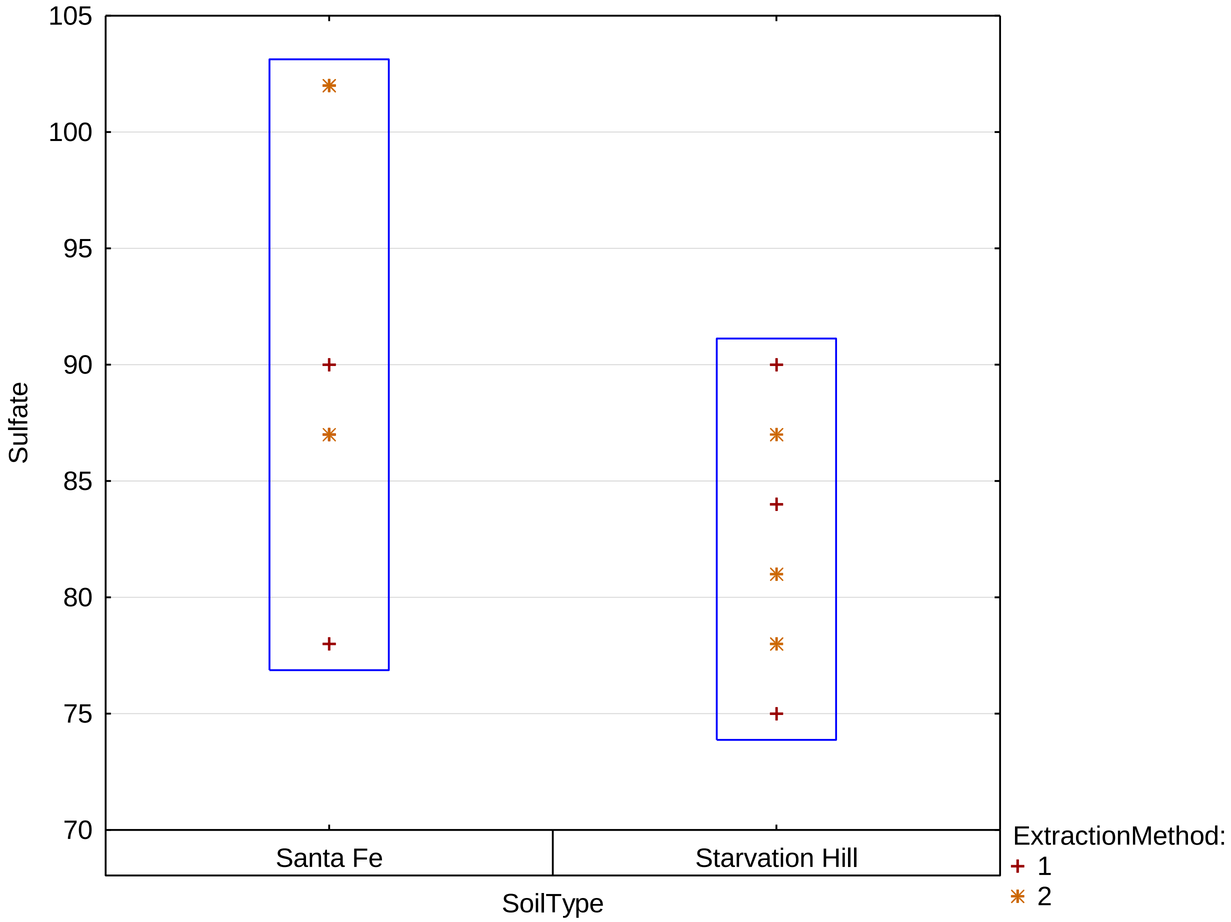


Figure 9-4. Variability plot of sulfate concentration (ppm) by soil type and extraction method.

Table 9-8 Comparison of Soil Sulfate Means by Soil Type and Extraction Method

Effect	Descriptive Statistics (Statistica Sulfate Spreadsheet)			
	Level of Factor	Number of Samples	Sulfate Mean (ppm)	Sulfate Std Dev (ppm)
Total		12	86.8	8.62
Soil Type	Santa Fe	6	91.0	9.42
Soil Type	Starvation Hill	6	82.5	5.61
Extraction Method	1	6	84.0	6.29
Extraction Method	2	6	89.5	10.3

Table 9-9 ANOVA for Soil Sulfate by Soil Type and Extraction Method

Effect	Fixed Effect Test for Sulfate (Statistica Sulfate Spreadsheet) Restricted Maximum Likelihood (REML) Type V decomposition			
	Num. DF	Den. DF	*F*	*p*
Soil Type	1	8	4.52	0.066
Extraction Method	1	8	1.89	0.206
Soil Type*Extraction Method	1	8	2.64	0.143

In summary, laboratory rather than field testing for sulfate concentration in soil is recommended to accurately measure soil mass and to prepare a sample extract that is sufficiently clear of particles and color that may interfere with the sulfate analysis. Of the two extraction method tested, both produced clear sample extracts with no detectable difference in sulfate concentration. Further testing of these two extraction methods on other soils is recommended.

9.2.5 Influence of meter/electrode system on pH measurement

Seen in the ruggedness study results for pH (Chapter 8, Section 8.3.2) that the FM for pH was sensitive to the electrode condition. This result also apparent from the laboratory visits (Chapter 6, Section 6.4.1). A new bench top pH meter and electrode system (Accumet AB150; 13-620-631) was purchased to compare with the portable system in current use (Accumet AP85; 13-620-AP55); both meters were recent mid-grade instruments with automatic temperature compensation (ATC) and visual display of electrode calibration slope and offset; both electrodes included indicating and reference electrodes plus a thermocouple (3-in-1 combination), were mercury-free with a silver/silver chloride reference electrode, had glass bulbs and an epoxy body. The bench top system had a double-junction electrode and the portable system had a single-junction electrode. The double-junction electrode was designed to extend the life of an electrode that measures pH in dirty solutions. The second pH meter/electrode system was received in time to make comparative measurements for Youngquist and Calhoun sands.

Twelve replicates of Calhoun sand were transported cool (~20°C), stored in a refrigerator (~4°C) for 5 d, quartered, brought to room temperature, and tested with the “as-received” moisture content. For the portable AP85/single-junction electrode system, after calibration the slope was 99.8%, offset 6.7 mV, and soil slurry temperature 23.3°C; for the bench top AB150, after calibration the slope was 97.4%, offset 10.1 mV, and soil slurry temperature 23.6°C. The samples were prepared with 100 mL of sand, 100 mL of DI water, stirred briefly at 10-min intervals over a 30-min period, and re-stirred just prior to measurement, as 12 samples took about one hr to test. Both electrodes were suspended in the sample and paired readings were taken simultaneously. Summary statistics are presented in Table 9-10 and data are graphed in Figure 9-5. The average pH measured by the AB150/double-junction electrode system was significantly higher than the average pH measured by the AP85/single-junction electrode system, based on a two-sided, paired t-test.

Table 9-10 Summary Statistics for pH in Calhoun Sand Using Two Different pH Meter/Electrode Systems

Statistic	AP85/13-620-AP55	AB150/13-620-631
Avg	4.64	4.88
St Dev	0.21	0.20
%RSD	4.61	4.01
%RE	18.5	15.2

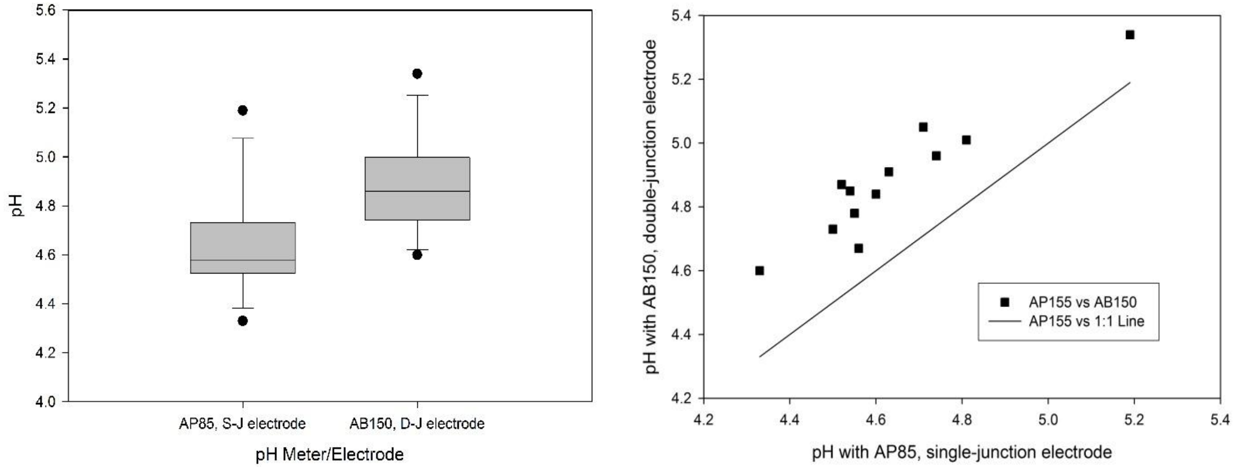


Figure 9-5. Comparison of two different pH meter/electrode systems for pH measurements in Calhoun sand.

In Figure 9-5, the box plots show moving from the center bar outward the median, 25th and 75th percentiles, 5th and 95th percentiles, and outliers, and revealed two important features of the data set: first, that pH measurements with the AP85 meter/electrode system were skewed and second, that the median values between the two systems were 0.28 pH units apart. In Figure 9-5, a plot of the 1:1 line shows that although the slopes of the two electrodes were similar, the double-junction electrode data points were on the average 0.24 pH units apart, while the difference of 3.4 mV in offset voltages predicted only 0.06 pH units (3.4 mV/59 mV/pH unit).

Twelve replicates of Youngquist sand were transported cool (~20°C), stored in a refrigerator (~4°C) for 7-9 d, quartered, brought to room temperature, and tested with the "as-received" moisture content. For the portable AP85/single-junction electrode system, after calibration the slope was 99.1%, offset 3.5 mV, and soil slurry temperature ~24.0°C; for the bench top AB150/double-junction electrode, after calibration the slope was 98.3%, offset 6.8 mV, and soil slurry temperature 24.2°C. The samples were prepared with 100 mL of sand, 100 mL of DI water, stirred briefly at 10-min intervals over a 30-min period, and re-stirred just prior to measurement, as 12 samples took about one hr to test. Electrodes were sequentially suspended in the sample and paired readings were taken about 5 min apart. Measurements were made on different days, with pH of six replicates measured on one day and six replicates measured two days later. Summary statistics were presented in Table 9-11 and data are graphed in Figure 9-6. The average pH measured by the AB150/double-junction electrode system was significantly higher than the average pH measured by the AP85/single-junction electrode system, based on a two-sided, paired t-test.

Table 9-11 Summary Statistics for pH in Youngquist Sand Using Two pH Meter/Electrode Systems

Statistic	AP85/13-620-AP55	AB150/13-620-631
Avg	8.15	8.34
St Dev	0.20	0.24
%RSD	2.51	2.89
%RE	7.40	8.60

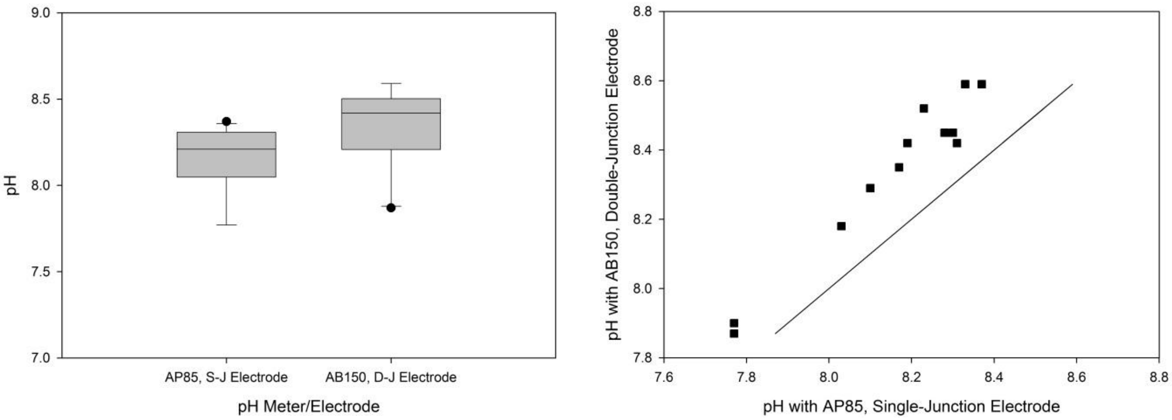


Figure 9-6. Comparison of two pH meter/electrode systems for pH measurements in Youngquist sand.

In Figure 9-6, the box plots show moving from the center bar outward the median, 25th and 75th percentile, 5th and 95th percentiles, and outliers, and revealed two important features of the data set: first, that pH measurements with both meter and electrode systems were skewed and second, that the median values between the two systems were 0.21 pH units apart. In Figure 9-6, a plot of the 1:1 line shows that although the slopes of the two electrodes were similar, the double-junction electrode data points were on the average 0.18 pH units apart, while the difference of 3.3 mV in offset voltages predicted only 0.06 pH units (3.3 mV/59 mV/pH unit).

The preliminary conclusion drawn from a comparison of pH meter/electrode systems is that even with pH meters/electrode systems in good working order, variability between systems may make a large contribution to the method reproducibility.

9.2.6 Effect of ionic strength adjustment on pH measurement

In low ionic strength solutions an increase in the voltage drop across the liquid junction of the reference electrode tends to bias high the pH measurement. The addition of a salt such as potassium chloride or calcium chloride can improve the speed and stability of the pH measurement by improving the transference of ions through the liquid junction to the bulk solution (Chapter 3, Section 3.2.1). In Figure 9-7 is illustrated the effect of potassium chloride addition on pH measurement for Santa Fe River sand and Jahna sand, two sands with low ionic strengths but with alkaline and acidic pH, respectively. Potassium chloride was added using a 0.05-mL spatula (and its mass monitored on an analytical balance) to 100 g of air-dried, sieved soil. To the soil was added 100 mL of deionized water and the soil solution was stirred briefly every 10 min for a 30-min period, after which time the pH was measured with the AB150/double-junction electrode. The electrode calibrations were 100% slope and 5.6 mV offset for pH 4 to pH 7 and 108% slope and 5.6 mV offset for pH 7 to pH 10. Soil solution temperatures were ~25.0°C. The pH dropped by ~0.5 pH units for Santa River sand and ~0.7 pH units for Jahna sand as potassium chloride was increased from 0.0 g to 0.5 g in 100 g soil; most of this drop occurred for a potassium chloride addition of 0.10 g to 100 g of soil (Figure 9-7). A measurement shift of ~0.5 pH units would likely disqualify some of Florida's sands as candidates for MSE wall backfill.

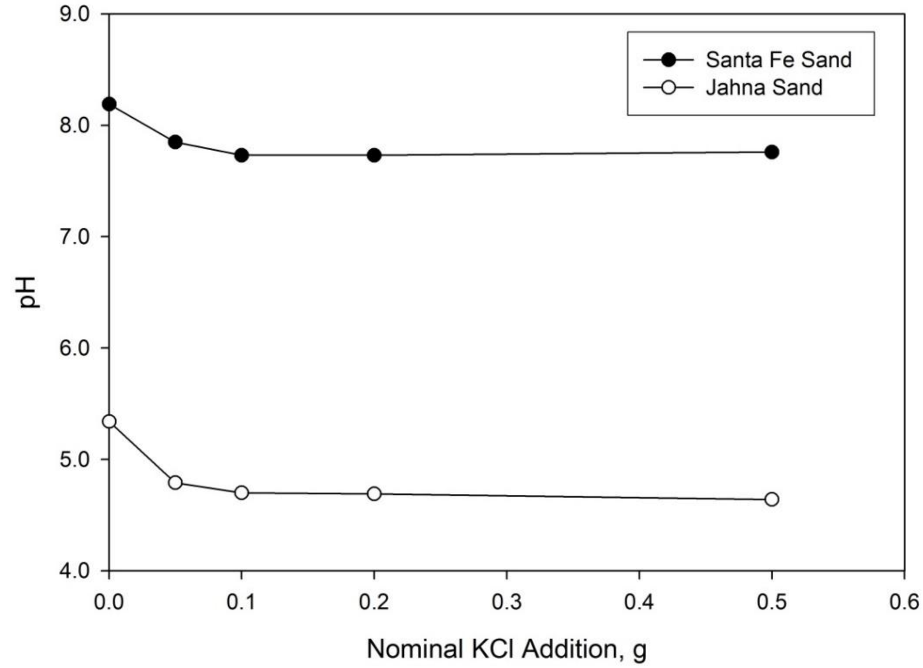


Figure 9-7. Effect of potassium chloride (KCl) addition on pH.

9.2.7 Potassium chloride versus calcium chloride to adjust ionic strength

There appears to be no controversy regarding the difficulty of accurate pH measurements in a water or soil solution with low ionic strength (Bier, 2009; Busenberg and Plummer, 1987; Miller and Kissel, 2010; Wolt, 1994). Bier (2009) recommended adding 0.1 g of potassium chloride to 100 mL of pure or tap water sample to improve the reading stability and notes that the pH reading will shift ~0.10 pH units in response to the salt addition. Observed in the USF laboratory was a shift in pH from~ 5.60 to ~5.50 with the addition of 0.1 g of potassium chloride to a deionized water sample; these pH readings, however, were quite noisy even with 0.10 g potassium chloride added. Busenberg and Plummer (1987) estimated that in low ionic strength water the error associated with the liquid junction potential was ~0.06 pH units; they also reported that adding potassium chloride to low ionic strength water improved the stability of pH readings. They argued against adding potassium chloride, however, because of their experience-based concern that potassium chloride salts or solutions were often contaminated and that contaminants may affect the pH readings.

Miller and Kissel (2010) maintained that 0.01 molar calcium chloride added to a 1:1 soil:water extract counteracts the measurement error associated with the liquid junction potential in a glass bulb-reference electrode system. They provided evidence for agricultural soils that a downward shift of ~1 pH unit occurs when a 1:1 soil:pure water extract was replaced with a 1:1 soil:0.01 molar calcium chloride extract. With an exception for acid soils, they argued against the theory that calcium chloride displaces protons on the soil surface, and based their argument on the amount of acid titrated in samples before and after salt addition. From a careful reading of Puri and Asghar (1938), the addition of potassium chloride to soil samples has the opposite effect as that of adding water to dilute the soil and its soluble salts; hence, potassium chloride addition drives the pH reading toward the *in-situ* pH. Observed in the laboratory was a downward shift of ~0.5 pH units with the addition of 0.1 g of potassium chloride to pH samples. Using calcium chloride instead of potassium chloride shifted the pH even lower by an average of 0.7 pH units for Alico Road sand and 0.4 pH units for Clermont sand (Chapter 8, Section 8.3.2). A significant decrease in soil pH standard deviation was seen in the fixed effect study (Section 9.2.1), but in ruggedness studies such decreases were not significant (Appendix A, Tables A-8, A-18, A-40, A-47); neither was a significant decrease seen in the replicate study (Chapter 11, Section 11.3.1).

Wolt (1994) wrote that adjusting the ionic strength of a soil solution can mitigate the pH change due to differences in the standard pH buffers and low ionic strength soil solutions. A standard pH buffer solution has a conductivity of ~7,000 µS/cm compared with a Sebring soil conductivity of ~30 µS/cm (conductivity is proportional to ionic strength). Purchased “low ionic strength” buffer solutions of pH 4.10 and pH 6.97 had at room temperature conductivities of 1,850 µS/cm and 2,010 µS/cm, respectively. In the USF soils laboratory, biases in pH measurements were small for low-ionic strength buffers as were differences between normal- and low-ionic strength buffers (Chapter 5, Section 5.2.2).

In summary, least four explanations were found for a downward shift in pH in soil solutions with the addition of potassium chloride or calcium chloride:

- The salt cations displaced protons from exchange sites on the soil surface;
- The salt cations displaced aluminum, iron, or manganese from exchange sites on the soil surface and these metals ions were hydrolyzed and released protons;
- There was a change in the liquid junction potential; and

- The typical pH electrode calibration failed in a low ionic strength solution.

The use of potassium chloride or calcium chloride to adjust the ionic strength of soil solutions during pH measurement was not recommended at this time. The observed downward shift in pH in sandy soils with neutral salt addition, however, may indicate that these soils have significant total acidity. Recommended was further investigation of the relationship between metal corrosion rates in select backfill and soil acidity, where soil acidity is determined as both proton activity (electrochemical pH measurement) and exchangeable acidity.

9.2.8 Effect of dilution water and slurry water content on minimum resistivity in soils

In this experiment the effect of dilution water resistivity and slurry water content on minimum resistivity in six sands was investigated. Slurry water content was tested because the FM for resistivity appeared to be sensitive to the amount of water transferred in slurry from the mixing bowl to the soil box (Chapter 8, Section 8.3.3). The sands tested were Calhoun (CA), Jahna (JA), Santa Fe (SF), Starvation Hill (SH), Wimauma (WI), and Youngquist (YO). Dilution water resistivity was tested at two levels, which were nominally 1,000,000 ohm-cm (no added salt) and 200,000 ohm-cm (added salt). The upper level represented the high end of the resistivity meter scale and the lower level represented the minimum resistivity for Type IV reagent water (ASTM D1193-06). Slurry water content was also tested at two levels, where the slurry content was predominately soil (SS) or predominately water (WS). For the sands tested, slurry typically formed when the water content exceeded 20%, but the nature of the slurry was different for sands with a greater proportion of fine particles such as the Santa Fe River and Youngquist sands. In these sands the boundaries between sand and water in the slurry were less distinct than seen for the larger-grained sands. To transfer mostly soil, a spoon was used and to transfer mostly water, water was decanted directly from the mixing bowl into the soil box and soil was spooned in as needed to fill the box.

All soils were dried either at room temperature or in an oven at a temperature not exceeding 60°C, sieved through a No. 10 sieve, and mechanically split to obtain 1000-g samples. Deionized (DI) water was obtained from the USF Nanotechnology Research and Education Center and at ~23^{o}C had a resistivity greater than 1,000,000 ohm-cm. Slightly-salted water with a measured resistivity of 175,000 ohm-cm was prepared by adding to the DI water 5.0 mg/L (ppm) of reagent-grade sodium chloride. Testing took place over three days.

Summarized in Table 9-12 are the average, standard deviation, %RSD, and %RE minimum resistivity across all four combinations of dilution water and slurry water content by sand; presented in Figure 9-8 are the corresponding 25th, 50th (median), and 75th percentiles. Disparate minimum resistivity results reported between laboratories in Table 7-2 (Chapter 7, Section 7.4) are now seen to be within two standard deviations of the average as shown in Table 9-12, or in other words, the between-laboratory variability can be explained by dilution water resistivity or slurry water content.

Table 9-12 Summary Statistics for Minimum Resistivity by Sand

Sand	Avg, ohm-cm	St Dev, ohm-cm	%RSD	%RE
Calhoun	64,900	35,300	54.4	104
Jahna	79,600	34,300	43.0	89.8
Santa Fe	12,800	7,160	56.0	116
Starvation Hill	22,900	12,900	56.3	103
Wimauma	38,900	21,700	55.9	108
Youngquist	7,900	2,020	25.6	55.7

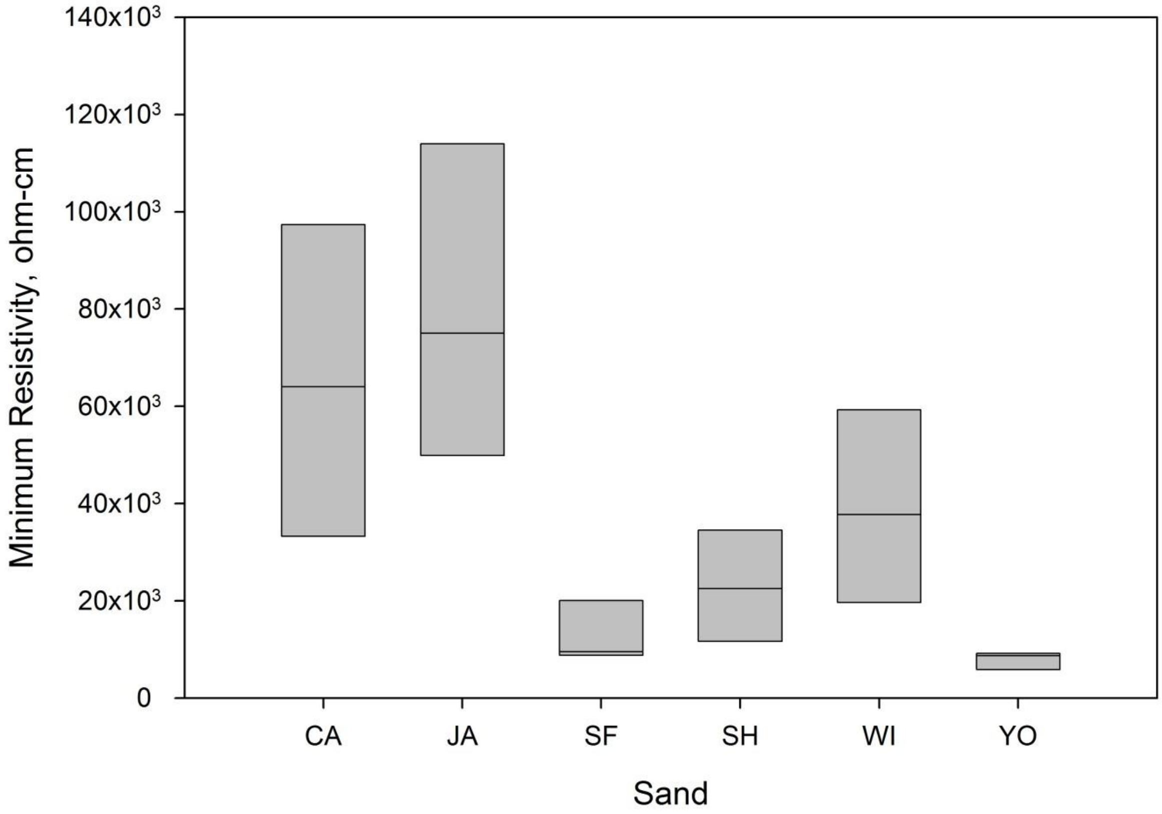


Figure 9-8. Variation in minimum resistivity by sand across two levels of dilution water resistivity and for slurry water content in the soil box that is either mostly sand or mostly water.

Tested at the 95% confidence level was the null hypothesis that the minimum resistivity mean and standard deviation were the same for a dilution water resistivity greater than 1,000,000 ohm-cm and a dilution water resistivity of 175,000 ohm-cm. Based on a *t*-test ($p = 0.67$) and an *F*-test ($p = 0.64$) the null hypotheses was not rejected (Figure 9-9). These results supported a recommendation to use Type IV reagent water (e.g., deionized or distilled water) with a resistivity of 200,000 ohm-cm or greater as dilution water for the FM for resistivity.

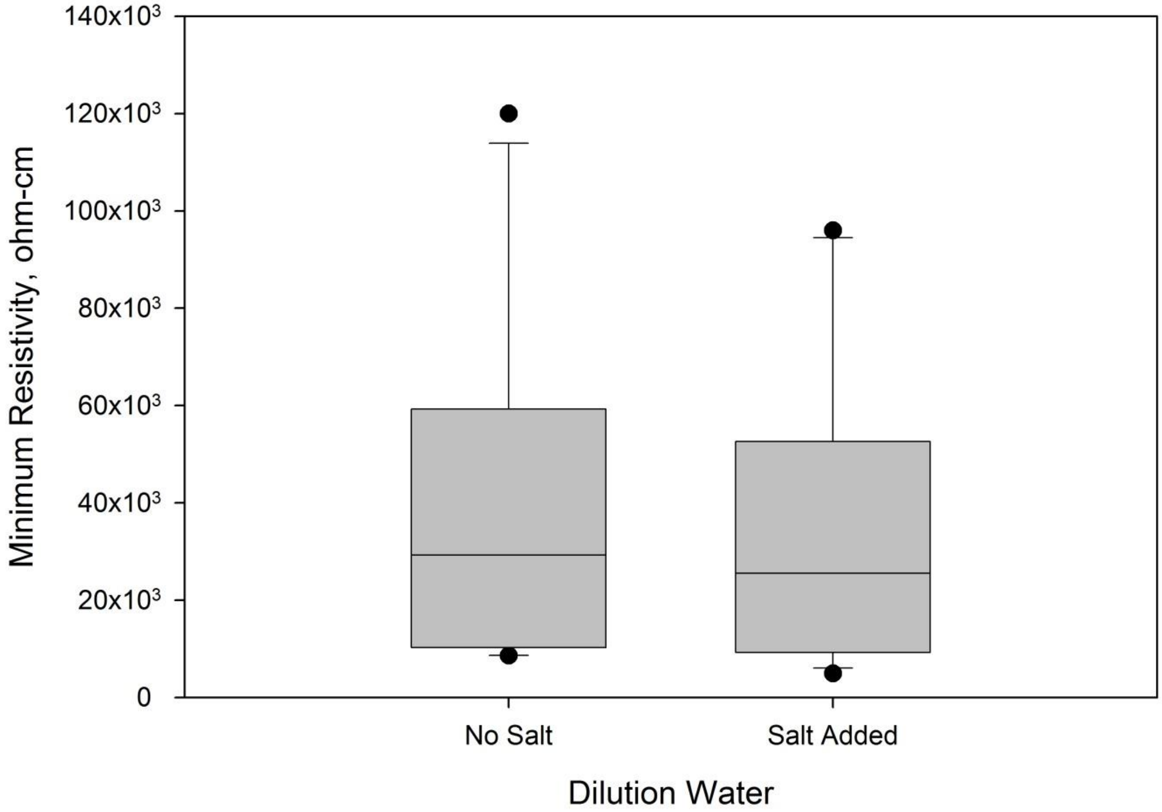


Figure 9-9. Variation in minimum resistivity by dilution water resistivity for six sands and for slurry water content in the soil box that is either mostly sand or mostly water.

Tested at the 95% confidence level was the null hypothesis that the minimum resistivity mean and standard deviation were the same for soil slurry placed in the soil box that is mostly sand or mostly water. Based on a *t*-test ($p = 0.021$) and an *F*-test ($p = 0.0074$) the null hypothesis was rejected (Figure 9-9). These results supported the recommendation to expand the FM for resistivity to include testing water decanted from soil slurry, where the slurry is formed during the test procedure. This recommendation is conservative, consistent with AASHTO T288, and intended to reduce the variability seen between laboratories.

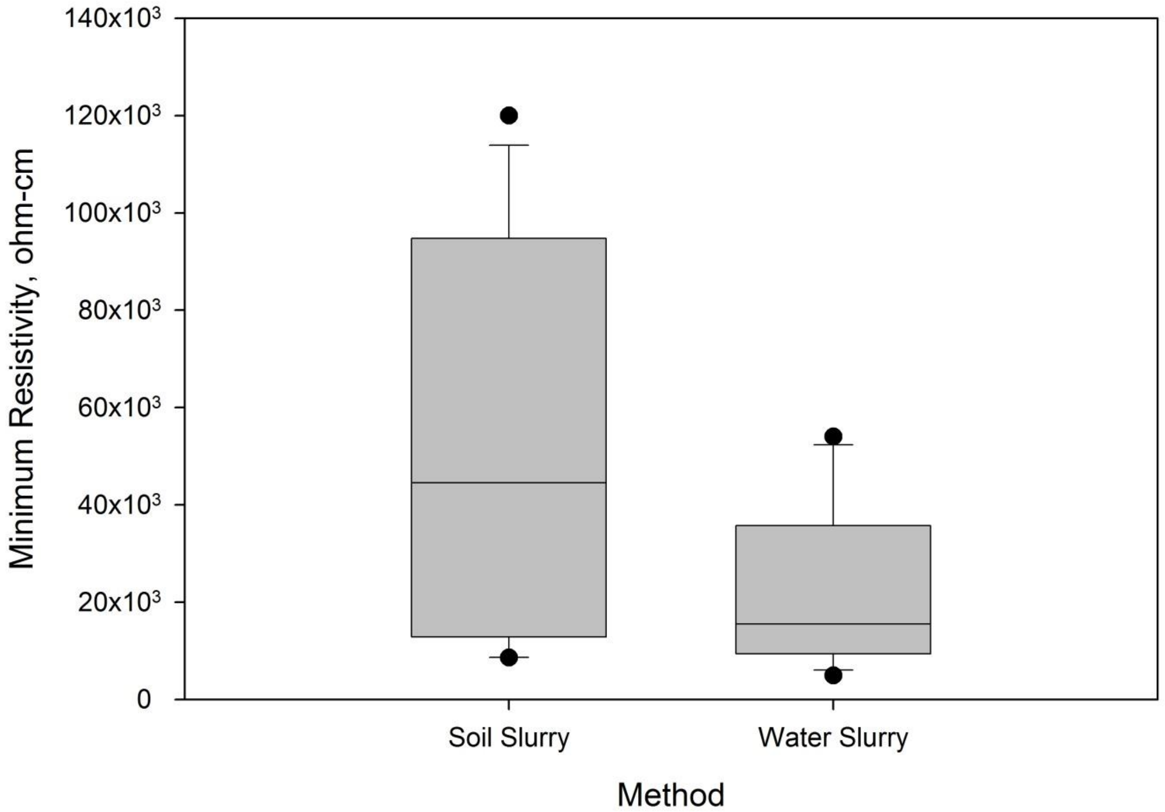


Figure 9-10. Variation in minimum resistivity by slurry water content for six sands and for dilution water resistivity between 200,000 and 1,000,000 ohm-cm.

9.2.9 Choice of range selection on sulfate measurements with a test kit

The current FM for sulfate lists as an apparatus the Hach Sulfate Photometer Test Kit (or equivalent), which upon purchase included not only an instruction manual and the photometer but two glass bottles and powder pillows of barium chloride reagent (SulfaVer 4) for 100 tests. The advantages of this kit are its affordability, small size (portability), rapid response, and ease of use. The photometer includes built-in calibration curves for sulfate, although a user can manually input a new curve. Even with the built-in calibration curves, however, a method operator should check one or more calibration standards to determine which range gives the best result. Figure 3-5 (Chapter 3, Section 3.5.3) shows that for the instrument the slope of the sulfate calibration curves were different between Range 1 and Range 2, and Range 2 was higher. Moreover, Figure 3-5 gives graphical evidence that the photometer response was lower for reagent lot A3303 than for A4120; reagent lot A3303 had been purchased six months earlier than lot A4120 and their respective expiration dates were October 2017 and April 2018, respectively. These results suggested that reagent potency was not consistent between lot numbers and possibly not consistent over time.

9.2.10 Soil conductivity

Field conductivity measurements were substituted for field minimum resistivity measurements. Conductivity measurements were made using a portable pH/mV/conductivity meter AP85 with automatic temperature compensation and a compatible temperature-sensing conductivity electrode. The electrode was calibrated in the field with a 250-µS/cm (4,000 ohm-cm) sodium chloride conductivity standard, and the minimum reading was checked using deionized water. Approximately 75 mL of sand was diluted with 150 mL of deionized water in a 250-mL beaker (Hanlon, 2009). Conductivity expressed as resistivity in ohm-cm was summarized for each soil in Table 9-13. Given a dilution factor of two for the conductivity (field) measurements, the results were in good agreement for Alico Road and Angelo's sand (ratio of 2); the results did not agree well, however, for Clermont and Sebring soils (ratios of ~8 and ~4, respectively). Note, however, that for Clermont and Sebring sands, the conductivities approached the detection limit of the conductivity meter. Further consideration of soil conductivity as a field screening method for minimum resistivity is recommended.

Table 9-13 Comparison of Conductivity (Field) and Minimum Resistivity (Lab)

Sand	Field Resistivity, ohm-cm	Lab Min Resistivity, ohm-cm	Ratio
Alico Road	23,600	11,200	2.11
Angelo's	38,900	17,800	2.18
Clermont	221,000	28,200	7.85
Sebring	134,000	36,100	3.88

9.2.11 Contribution to pH by minerals retained on a No. 10 sieve

For Alico Road sand, a significant fraction of sand was retained on a No. 10 sieve. For replicate samples of this sand (Chapter 11), both passing and retained fractions were weighed, and the relative contribution of the retained fraction was calculated, as shown in Table 9-14. (AASHTO T288 provides guidance for separating and testing the fraction retained on a No. 10 sieve.) The pH was also determined in both fractions; for the retained fraction, however, pH measurements were made with 30 g of soil and 30 g of deionized water, as not all samples had 100 g. The combined pH was predicted by apportioning the measured pH to passing and retained fractions; for the two samples that were inadvertently discarded, an average pH of 9.10 was used instead. Note that none of the Alico Road predicted values were greater than pH 9.00 (Table 9-14), but treatment study samples transported under ambient conditions, stored at room temperature, and tested "as received" were greater than pH 9.0, which suggested that some alkalinity was lost in the drying process. Based on these results, testing "as received" soil for pH was recommended.

Table 9-14 Contribution of Mineral Fraction Retained on a No. 10 Sieve to Total Mass and pH

Replicate	Passing, g	Retained, g	Total, g	Retained, %	pH Passing	pH Retained	pH Predicted
1	2,962	134	3,095	4.3	8.86	9.16	8.87
2	2,854	178	3,032	5.9	8.87	9.17	8.89
3	2,904	141	3,045	4.6	8.88	9.14	8.89
4	3,103	296	3,399	8.7	8.86	9.16	8.89
5	2,775	223	2,998	7.4	8.89	9.01	8.90
6	2,930	93	3,024	3.1	8.88	9.03	8.88
7	3,183	361	3,545	10	8.88	9.11	8.90
8	3,067	145	3,212	4.5	8.81	9.08	8.82
9	2,796	185	2,981	6.2	8.84	-	8.86
10	3,009	149	3,159	4.7	8.89	9.08	8.90
11	2,366	676	3,042	22	8.85	-	8.91
12	2,836	162	2,997	5.4	8.90	9.02	8.91
Averages	2,899	229	3,127	7.3	8.87	9.10	8.88

9.3 Summary

For pH measurements in sieved soils, the pH changed for soil with a significant mass retained on the sieve; by inference in some soils under similar circumstances the minimum resistivity could also change. AASHTO T288 requires the soil be sieved for a minimum resistivity measurement but provides guidance for separating and testing the fraction retained on a No. 10 sieve. For both pH and minimum resistivity, the current practice of testing soils "as received" was recommended. For one soil, the average pH measurement was significantly lower for warm transport and storage than for cool transport and cold storage; across all four soils the average pH observations were in reasonable agreement between measurements made on-site and those made in the laboratory for soils transported cool and stored cold. Treatment study results also suggested that variability in sample minimum resistivity between laboratories could be reduced if laboratories processed samples in a similar manner, for example, with transport under ambient conditions and samples stored at room temperature. To reduce variability in sulfate concentrations measured between laboratories, amending the FM to allow drying the soil from room temperature up to 60°C, consistent with the AASHTO T290 drying temperature, was recommended.

Some sands that met the specifications for MSE wall backfill had high minimum resistivity (low conductivity) and thus low ionic strength, and were a challenge for pH measurements. Potassium chloride, a neutral salt, is a possible amendment to soil samples for pH testing. Three advantages to the addition of 0.1 g of potassium chloride to 100 g of soil sample were: the pH reading was faster, more stable, and was more likely to better represent the *in-situ* soil pH; the major disadvantage, however, was a drop of ~0.5 pH units in 1:1 soil:water solutions. Such a shift would likely disqualify some of Florida's sands as candidates for MSE wall backfill. The use of potassium chloride or calcium chloride to adjust the ionic strength of soil solutions during pH measurement was not recommended at this time. The observed downward shift in pH in sandy soils with neutral salt addition, however, may indicate that these soils have significant total acidity. Recommended was further investigation of the relationship between metal corrosion rates in select backfill and soil acidity, where soil acidity is determined as both proton activity (electrochemical pH measurement) and exchangeable acidity.

A comparison of pH meter/electrode systems revealed that even with pH meters/electrode systems in good working order, variability between electrodes may make a large contribution to the method (im)precision.

Research results supported the recommendation to use Type IV reagent water (e.g., deionized or distilled water) with a resistivity of 200,000 ohm-cm or greater as dilution water for the FM for resistivity and to expand the FM for resistivity to include testing water decanted from soil slurry, where the slurry is formed during the test procedure. This recommendation was conservative, consistent with AASHTO T288, and intended to reduce the variability seen between laboratories. Results of soil conductivity as a field screening method were encouraging but were based on low and very low conductivity soils. Further consideration of conductivity as a screening tool was recommended. For both the FMs for chloride and sulfate, laboratory rather than field testing was recommended to accurately measure soil mass; moreover, soil extracts must be clear of suspended particles and color that may interfere with analyses. After gravity filtration through a coarse fast filter, vacuum filtration of soil extract through a 0.45-micron membrane filter was recommended. Finally, for the FM for sulfate (Hach test kit method), research results suggested that reagent potency was not consistent between lot numbers and possibly not consistent over time. The relationship between lot number and sulfate calibration curve should be checked prior to a sample measurement.

10 Inter-Laboratory Study

10.1 Scope and Purpose of Study

The purpose of this study was to estimate a multi-laboratory precision (reproducibility) for the revised methods, and to the extent practicable the study was designed in accordance with ASTM C802. Over a three-day period, each participating laboratory analyzed two select backfill (FDOT 092L) materials for pH, minimum resistivity, chloride, and sulfate per proposed revised FMs. Results for each material were aggregated to produce an estimate of between-laboratory variances and, consistent with ASTM C670, a precision statement was prepared to accompany each of the revised methods. ASTM C802 recommended that each material be tested in duplicate for 10 or more laboratories and with higher replication for fewer laboratories to obtain an estimate of within-laboratory variability. FDOT's corrosion series methods require a single test rather than replicate tests for the reported test result and routine comparisons of within-laboratory replicate results were not made (in practice, a laboratory re-ran a sample if results were unusual). Moreover, material properties affected test results for one or more methods; for example, the presence of colloidal particles interferes with both pH and sulfate determinations. For this reason, two different materials rather than replicates of one material were tested to obtain two estimates of the between-laboratory precision at the expense of the within-laboratory precision.

Participating laboratories included five FDOT district laboratories in Bartow, Chipley, Davie, Deland, Lake City; the FDOT State Material Office laboratories in Gainesville, and the USF soils laboratory in Tampa. Each laboratory was assigned at random a number between 1 and 7, which was not shared, and results were reported by laboratory number. Laboratory personnel were given training on the proposed revised methods ahead of the study date. Each laboratory received in advance of the study a study plan (Appendix C), with a data sheet and the proposed revised FMs attached. Both paper and electronic documents were provided. The proposed revisions updated and expanded the methods' procedural details and included changes to method equipment, sample processing, and data management.

The results of the first inter-laboratory study indicated that further work on the FM for pH was needed. At the USF soils laboratory, study conditions were mimicked and revealed that a memory effect likely contributed to dispersion in the pH results; this effect was pronounced between samples of disparate pH values, for example, pH 7 and pH 9. The method was revised and a second inter-laboratory study was conducted for pH for two samples, each in duplicate. Refer to Appendix C for the study plan and data sheet for the second study.

10.2 Sample Preparation

Material A was characterized by the mining operator as mine tailings. The sand fizzed when a few drops of 10% hydrochloric acid were added to a ~1-g subsample, which indicated the presence of carbonates. Material B was characterized by the mine operator as mason's sand; the presence of carbonate was not detected in this sand. Both sands had ~30% of its mass passing a

No. 100 (0.15 mm) sieve; with 3.4 % and 0.25% passing a No. 200 (0.075 mm) sieve for Material A and B, respectively. For Material B, however, 3:1 water-to-soil extracts were poorly settled even after 24 hr, which suggested the presence of colloidal particles (particles with a diameter in the range of 0.001 to 0.10 µm). Both Material A and B as sampled had chloride and sulfate concentrations below their respective method detection limits. Material A was not amended with salts but to Material B was added 0.01% by weight sodium chloride for a target chloride concentration of 61 ppm and 0.01% by weight sodium sulfate for a target sulfate concentration of 81 ppm. The anticipated minimum resistivity of Material B was ~3000 ohm-cm based on the added salts alone.

Soils were dried in an oven at 60°C and sieved through a No. 10 (2 mm) mesh upon receipt at USF from the mines (see Table 1-1 for sampling dates) and stored at room temperature in a covered plastic bucket. Material A was from Mine 8 (Alico Road sand) and Material B was from Mine 2 (Jahna sand). In mid-December 2014, Material A was mechanically split into ~1,500-g samples; salts were added to Material B in 3-kg batches, and these batches were placed under a mixer on low speed for 10 minutes, then combined and mechanically split to ~1,500-g samples. For both materials, samples were placed in numbered and sealed plastic bags, stored in covered plastic buckets, and delivered to participating laboratories by automobile. Samples likely experienced modest temperature swings during the course of their transit.

For the second pH inter-laboratory study Material C was an acid sand from Mine 6 (Sebring sand) and Material D was a mason's sand from Mine 7 (Clermont sand). Soils were dried in an oven at 60°C and sieved through a No. 10 (2 mm) mesh upon receipt at USF from the mines (see Table 1-1 for sampling dates) and stored at room temperature in a covered plastic bucket. For both materials, samples were mechanically split to ~300 g, placed in numbered and double-wrapped in sealed plastic bags, and were shipped by US Postal Service priority mail to arrive at participating laboratories ~1 week before the March 2015 start date.

10.3 Data Management

Data was handled and reported as required by the revised FMs, with exceptions as noted on the data sheet (Appendix C). Measurements that were below detection were to be flagged as such. Upon completion of testing, the data sheets were electronically submitted to the study contact.

10.4 Results and Discussion

Study results were presented in Table 10-1. For Material A, the average (± standard deviation) values for each method were pH, 9.19 ± 0.07; minimum resistivity, 12,200 ± 1,090 ohm-cm; chloride, 7 ± 8 ppm, and sulfate: 4 ± 4 ppm. Consensus values (average and median) for chloride and sulfate were below the stated method detection levels of 15 ppm and 6 ppm for Hach-kit chloride and sulfate, respectively, when expressed as a soil concentration. For Material B, the average (± standard deviation) values for each method were pH: 7.02 ± 0.72; minimum resistivity, 2,310 ± 430 ohm-cm; chloride, 66 ± 12 ppm; and sulfate, 67 ± 16 ppm. For Material

B, the relative standard deviations (%RSD) and relative error (%RE) were much higher for pH and resistivity and much lower for chloride and sulfate than for Material A. For chloride and sulfate the improvement in %RSD and %RE can be explained by concentrations above their corresponding detection levels. Recoveries for added chloride and sulfate were 99% and 83%, respectively.

Table 10-1 Inter-Laboratory Study Results for Proposed Revised FMs for pH, Minimum Resistivity, Chloride and Sulfate

Lab	Material A				Material B			
	pH	Resistivity, ohm-cm	Chloride, ppm	Sulfate, ppm	pH	Resistivity, ohm-cm	Chloride, ppm	Sulfate, ppm
1	9.15	12,500	0	0	6.88	2,200	60	87
2	9.11	13,000	15	3	6.33	2,700	60	39
3	9.31	11,800	15	9	6.46	2,360	90	72
4	9.24	11,000	0	3	6.85	2,300	60	54
5	9.13	12,000	0	3	6.97	2,600	60	69
6	9.18	14,000	15	1	7.63	2,600	75	75
7	9.18	10,950	3	10	8.39	1,420	57	70
Avg	9.19	12,200	7	4	7.07	2,310	66	67
St Dev	0.07	1,090	8	4	0.72	433	12	16
Median	9.18	12,000	3	3	6.88	2,360	60	70
%RSD	0.8	9.0	110	93	10	19	18	23
%RE	2.2	25	220	240	29	55	50	72

For pH, if we assume that the method instrumentation, operator, and measurement temperatures were the same for both materials, then the difference seen in reproducibility between the two materials were likely related to material properties. Since salt was added to Material B, effects due to low ionic strength were ruled out. Four possible explanations were:

- The liquid junction of the pH electrode trapped a portion of the previous sample or buffer. If this occurred, the current pH reading would be distorted until the liquid junction re-equilibrated with the current sample;
- Colloidal particles were present in the sample and interfered with the voltage drops on both the glass bulb and in the liquid junction; and
- For an un-buffered material at pH 7.0, if the proton (H^+) concentration in solution was close to that in gel layers on the inside and outside of glass bulb surfaces, the electrode response was unstable.
- The space between the glass bulb and thermocouple trapped a small amount of the previous sample, buffer, or rinse water and thus affected the pH reading.

The FM for pH was revised to include steps to mitigate the memory effect, and included (1) directions to disable the hold feature of the pH electrode, (2) steps to re-check electrode calibration in a pH 7 buffer between samples, and (3) a second dilution water rinse and re-test of pH within each sample. Results of the second pH inter-laboratory study were reported in Tables 10-2 and 10-3. The pH averages, standard deviations, and %RSDs were given in Table 10-4; estimates of within- and between-laboratory standard deviations were calculated according to ASTM C802.

Table 10-2. Material C Results Revised FM for pH

Laboratory	Material C			
	Replicate 1	Replicate 2	Avg	St Dev
1	8.23	8.29	8.26	0.04
2	7.62	7.69	7.66	0.05
3	7.64	7.67	7.66	0.02
4	7.44	7.56	7.50	0.08
5	7.67	7.68	7.68	0.01
6	7.37	7.48	7.43	0.08
7	8.14	8.12	8.13	0.01
Avg	7.73	7.78	7.76	0.04
St Dev	0.33	0.30	0.32	-

Table 10-3. Material D Results Revised FM for pH

Laboratory	Material D			
	Replicate 1	Replicate 2	Avg	St Dev
1	5.20	5.06	5.13	0.10
2	5.06	5.12	5.09	0.04
3	4.81	4.86	4.84	0.04
4	5.11	5.12	5.12	0.01
5	5.29	5.22	5.26	0.05
6	5.04	5.09	5.07	0.04
7	5.27	5.24	5.26	0.02
Avg	5.11	5.10	5.11	0.04
St Dev	0.17	0.13	0.14	-

Table 10-4 pH Averages, Standard Deviations, and %RSD

Material	Average	Standard Deviations		%RSD	
		Within Lab	Between Labs	Within Lab	Between Labs
C	7.76	0.051	0.32	0.66	4.09
D	5.11	0.049	0.15	0.97	2.86

An improvement in method precision for pH was seen from the first to the second inter-laboratory study, but the between-laboratory precision for Material C was double that of Material D. Within-laboratory precision for both sands were ~0.05 pH units. Both soils had relatively high minimum resistivity (Chapter 9, Section 9.1.1, Table 9-1) or low conductivity and thus low ionic strength, and low ionic strength coupled with a lower proton concentration likely contributed to the greater dispersion in pH values seen for Material C. Recall from Chapter 5 (Section 5.1.1) that within-laboratory precision typically represents the random component of analytical testing error and between-laboratory precision the systematic component of error. Overall the inter-laboratory results suggested that progress was made in reducing the systematic component of error.

10.5 Method Precision Statements

10.5.1 Precision statement FM for pH

For two test materials, multi-laboratory standard deviations of a single test result were dependent on the material (Table 10-5). For materials of similar pH, the results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than the pH units shown in column labeled “Acceptable Range of Two Results.”

Table 10-5 Multi-Laboratory Precision for FM for pH

Material	Avg	St Dev	Acceptable Range of Two Results
Sand (A-3)	7.76	0.32	0.91
Sand (A-3)	5.11	0.15	0.42

10.5.2 Precision statement FM for minimum resistivity

For two test materials, multi-laboratory standard deviations of a single test result were dependent on material (Table 10-6). For materials of similar minimum resistivity, the results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than the ohm-cm shown in column labeled “Acceptable Range of Two Results.”

Table 10-6 Multi-Laboratory Precision for FM for Minimum Resistivity

Material	Avg, ohm-cm	St Dev, ohm-cm	Acceptable Range of Two Results
Sand (A-3)	12,200	1,090	3,090
Sand (A-3)	2,310	430	1,230

10.5.3 Precision statement FM for chloride

For a test material (sand, A-3) with an average chloride concentration of 66 ppm, the multi-laboratory standard deviation of a single test result has been found to be 12 ppm. Therefore, results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than 34 ppm.

10.5.4 Precision statement FM for sulfate

For at test material (sand, A-3) with an average sulfate concentration of 67 ppm, the multi-laboratory standard deviation of a single test result has been found to be 16 ppm. Therefore, results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than 45 ppm.

10.6 Summary

Precision of pH, minimum resistivity, chloride, and sulfate measurements in candidate materials for select backfill were dependent upon the material. Relative standard deviations (%RSDs) for pH measurements were higher for a near-neutral mason’s sand than for a pH 9 carbonate-bearing sand or a pH 5 acid sand. Improvement in method precision for pH was seen between the first and second inter-laboratory study, and the latter featured pH method revisions that were intended to reduce electrode memory effects. Relative standard deviations (%RSDs) of chloride and sulfate measurements were much higher in a material with concentrations near the detection level than for concentrations of ~70 ppm, which was expected.

11 Replicate Study and Implications for Quality Assurance

11.1 Introduction

Distributions of pH, minimum resistivity, chloride, and sulfate were determined within and between soil mines for soils that qualify as select backfill and from these statistics were derived method operating characteristic (OC) curves. Sampling of select backfill takes place when a material is certified for this use at its source and again upon its emplacement behind an MSE wall. At the source, backfill from different locations in the strata or stockpile may be placed in a smaller stockpile from which samples are collected and composited for testing. At the construction site, independent tests of backfill are made after emplacement at least twice for each soil type: once for quality control by the project contractor and once for verification by the project engineer. Soil type is determined not only by visual inspection, but by other physical test results such as optimum moisture content and particle size distribution. If a backfill fails any one of the four corrosion tests, the backfill is tested a third time for resolution by an FDOT District Materials Office, State Materials Office, or their representative. Refer to Chapter 2, Section 2.2.3, for further explanation.

11.2 Methods

11.2.1 Field sampling

Soil samples were collected from eight different mines as listed in Table 1-1 (Chapter 1, Section 1.2.7); all samples were classified as sand (AASHTO A-3) and all samples met the geotechnical requirements for select backfill (FDOT material 092L) (Chapter 7, Section 7.3, Table 7-1). Of the eight mines, five mines were located in FDOT's District 1, two in District 7, and one in District 5. Mines included both dry pit and dredged strata, and samples were taken from a mine floor (one mine), mine walls (two mines), and stockpiles (five mines), two of which were mine tailings and two of which were size-segregated as mason's sand. Of the eight soil mines one was in Clermont, one in Dade City, two in Ft. Myers, two in Haines City, one in Sebring, and one in Wimauma. Each mine was identified by numerical sequence (1 to 8) in order of sampling date, because sample processing and analysis changed between samples collected from the first four mines and last four mines.

Mines were chosen by selecting names at random from a list of 30 sources that had one or more samples previously accepted for select backfill according to a FDOT Districts 1 and 7 Materials Office database. An attempt was made to contact each of these sources. Many of these mines were defunct, had changed ownership and no longer supplied select backfill, or did not respond to a telephone and/or e-mail inquiry. Seven of the eight mines sampled, however, were a subset of initial list.

Sampling was subject to selection bias because of the practical limits on geographical coverage, pre-selected characteristics of the soil, and accessibility of soil in stockpiles or soil strata in pits, and the results reported herein were not fully representative of Florida's resources. Soil sampling was more systematic than random or stratified random. The reported soil sample standard deviations include contributions from material, sampling, processing, environment, and analysis (Chapter 2, Section 2.2.1, Equation 2-4), where analyses were accomplished by USF soils laboratory.

At the Wimauma mine a backhoe operator dug 12 holes about 3-m deep in a grid pattern with holes spaced roughly 50 m apart. From each excavated soil pile, a ~3-kg soil sample was collected with a shovel and placed in a sealable plastic bag. The 12 samples were transported in a cooler on ice back to the USF soils laboratory. Soil from the remaining mines came either from a subsample of a stockpile or a pit wall and the sampling protocol was the same. At each of these mines an equipment operator removed one front loader bucket of soil from three separate locations near the base of the stockpile or pit. The three loads were kept separate but placed one next to the other; the tops of the soil piles were flattened with the back of the front loader bucker. From each of the three small soil piles were collected with a shovel four ~3-kg samples spaced roughly equidistant from each other for a total of 12 samples; each sample was placed in a separate sealable plastic bag. These 12 samples were transported in a cooler on ice back to the USF soils laboratory.

11.2.2 Sample processing

Samples were processed in accordance with FMs for pH, minimum resistivity, chloride, and sulfate. Samples were placed in new plastic bags and the bag was rolled down to reduce the air pocket between the sample and the bag seal. Sealed bags were arranged in a cooler and kept cool by frozen bottled water or ice packs, such that the transport temperature was typically 10 to 15°C cooler than ambient midday temperatures of 26 to 33°C. No samples were saturated with water, so removal of excess water was not an issue.

Upon receipt at the USF soils laboratory, samples collected from mines 1 through 4 were stored in a refrigerator at 4°C, quartered, with a portion brought to room temperature for pH and resistivity analysis and a portion dried for ~4 hr at 110°C for chloride and sulfate analysis. Once dried, the latter portion was stored at room temperature (~23°C). For samples collected from mines 5 through 8, samples were dried at 60°C for ~ 4 hr, sieved through a No. 10 (2 mm) mesh, and stored at room temperature prior to tests for pH, minimum resistivity, chloride, and sulfate.

11.2.3 Sample analysis

In addition to soil processing, analytical procedures also changed for pH and resistivity between samples collected from mines 1 through 4 and mines 5 through 8. For pH, a portable pH meter with a single-junction electrode was switched to a bench-top pH meter and a double-junction electrode, 100 g of dried and sieved soil was tested instead of 100 mL of soil at the "as received" moisture content, and 0.1 g of potassium chloride was added to each beaker that contained 100 g of soil and 100 mL of water. For minimum resistivity, 1,000 g of dried and sieved soil was tested instead of 1,000 g of soil at the "as received" moisture content, and the water portion rather than the soil portion of the soil/water slurry was preferentially tested. For chloride and sulfate, samples from mines 1 through 8 underwent an additional filtration step to clarify the sample extracts as necessary prior to analysis by chemical methods, as otherwise the interference from suspended particles and color was significant.

11.2.4 Data analysis

For pH, minimum resistivity, chloride, and sulfate, the central tendencies and data dispersion were presented with descriptive statistics such as the mean, median, and mode, standard error and standard deviation, as well as with box plots. In each box plot, the center line of the box represented the data's median, the box lower and upper boundaries represented the 25th and 75th percentiles, respectively, the box lower and upper whiskers represented the 5th and 95th percentiles, respectively, and the data points represented any outliers. The hypothesis was tested based on a one-sample Lilliefors-corrected Kolmogorov-Smirnov (K-S) test at the 95% confidence level (IBM SPSS Statistics 22) that the data distributions were not different from either a normal or a uniform distribution. The latter distribution was considered because (1) more than one mine separated material stockpiles by size, and (2) the potential for an unbroken geological stratum to have consistent geological and chemical properties.

A single-factor analysis of variance (ANOVA) was performed on each of the four datasets to assess the between- and within-sample variance (Appendix D). The within-sample variance was used as an estimate of the total variance σ_{total}^2 (Equation 2-4). This estimate, however, was for analysis by a single laboratory; to expand σ_{total}^2 for analysis by multiple laboratories, the single-laboratory variance was subtracted from and the multiple-laboratory variance added to the total variance. The single-laboratory variance was obtained from triplicate treatment study measurements for a treatment where sample processing and analyses were similar to that for the replicate study (Chapter 9, Section 9.3). The multi-laboratory variance was obtained from the results of an inter-laboratory study (Chapter 10, Section 10.4).

For the operating characteristic (OC) curves, the Type II (β) error was calculated according to Equations 11-1 (minimum resistivity, chloride, and sulfate) and 11-2 (pH). The inverse of the standard normal cumulative distribution function (NORM.S.INV, Microsoft Excel 2010) was used to determine $|z_\alpha|$or $|z_{\alpha/2}|$, where the Type I (α) was assigned as $p = 0.01$ (Table 2-7), and β was obtained from the standard normal distribution functions at z (NORM.S.DIST, Microsoft Excel 2010). In Equations 11-1 and 11-2, μ_0 is the rejection limit, μ_a the acceptance limit, σ the method test error estimated by$\sqrt{\sigma_{total}^2}$, and N the sample size (Burati et al., 1995; Ott, 1993).

$$\beta = P\left[z < z_\alpha - \frac{|\mu_0 - \mu_a|}{\sigma/\sqrt{N}}\right] \qquad (11\text{-}1)$$

$$\beta \approx P\left[z < z{\alpha/_2} - \frac{|\mu_0-\mu_a|}{\sigma/_{\sqrt{N}}}\right] \tag{11-2}$$

Between the source and the construction site, the process of mining, loading, transporting, stockpiling, and emplacing soil likely enhances soil mixing and improves the uniformity of emplaced material. For non-uniform soils, however, such mixing may yield a different average property than an average of individual samples collected from a relatively undisturbed source. To assess the influence of soil mixing on its measured properties, the mean and variance of individual soils from replicate studies were compared with the mean and variance of the same soils from treatment studies. For the treatment and other studies, ~100 kg of source material was composited on site and divided into smaller subsamples for sample handling (Chapter 7, Section 7.2). The sample handling and analysis protocols for replicate studies were matched with those of the treatment studies. To compare means, a two-tailed *t*-test with unequal variances was applied at the 95% confidence level ($p < 0.05$), where $\bar{x}_1$ and $\bar{x}_2$ were sample means for replicate and treatment studies, respectively. The null and alternative hypotheses were

$$H_0: \bar{x}_1 - \bar{x}_2 = 0 \tag{11-3}$$

$$H_1: \bar{x}_1 - \bar{x}_2 \neq 0 \tag{11-4}$$

To compare variances, an *F*-test was applied at the 95% confidence level ($p<0.05$), where s_1^2 and s_2^2 were sample variances for replicate and treatment studies, respectively. The null and alternative hypotheses were

$$H_0: s_1^2 = s_2^2 \tag{11-5}$$

$$H_1: s_1^2 > s_2^2 \tag{11-6}$$

11.3 Results

11.3.1 FM for pH

11.3.1.1 Distribution of pH in mined soil

In Table 11-1 were presented the descriptive statistics and in Figure 11-1 the box plots for soil pH within and between samples collected from eight mines. For MSE wall backfill reinforced with metal, backfill must have a pH between 5.0 and 9.0; for backfill reinforced with synthetic material, backfill must have a pH between 4.5 and 9.0 (Chapter 2, Section 2.1.2, Table 2-2). A single-factor analysis of variance (ANOVA) revealed that the variability of pH was greater between than within soils ($p = 0.00$) and the hypothesis that pH averages were equal across the eight soils was rejected (Appendix D, D.1, Table D-1). There was no clear evidence—either for central tendencies (*t*-test, $p = 0.06$) or dispersion (*F*-test, $p = 0.07$)—that differences in sample processing and analyses between the first four and the last four mines affected pH measurements within each soil (Figure 11-1). The pH in replicates from across all mines ranged from 4.00 to 8.90, with an average (± standard deviation) of 6.08 (± 1.68) and at the 95% confidence level, the average pH was between 5.74 and 6.42. The hypothesis that the distribution of replicate pH measurements was normal was not rejected for soil from all mines except mine 2; the hypothesis that the distribution of replicate pH measurements was uniform was not rejected for soil from all mines except mines 2 and 5. The mean (average), median, and mode (if present) pH from samples of soils from mines 1, 4, 5 and 6 were below pH 5.0 but above pH 4.5, and no soils had an average pH above pH 9.0. Standard deviations ranged from 0.025 to 0.63 pH units; all but the soil from mine 6 had standard deviations at or below 0.22 pH units. Kurtosis (peakedness) and skewness of the distributions is significant when these values exceed ± 2.0, for example, as seen for mine 2, and may reflect an impact of geological or industrial processes such as size segregation on the uniformity of pH in source material.

Table 11-1 Descriptive Statistics for pH

Statistic	Mine Identifier								
	1	2	3	4	5	6	7	8	All
Mean	4.66	5.37	8.15	4.88	4.65	4.70	7.40	8.87	6.08
Standard Error	0.025	0.064	0.059	0.057	0.059	0.183	0.022	0.007	0.170
Median	4.66	5.30	8.21	4.86	4.59	4.56	7.42	8.88	5.26
Mode	4.70	5.30	7.77	none	4.46	none	7.47	8.88	8.88
Std Deviation	0.087	0.220	0.204	0.196	0.204	0.634	0.077	0.025	1.68
Sample Variance	0.008	0.049	0.042	0.038	0.042	0.401	0.006	0.001	2.81
Kurtosis	-0.64	6.79	0.32	1.70	2.02	1.76	-1.08	1.11	-1.38
Skewness	0.40	2.47	-1.16	0.93	1.38	1.26	-0.09	-1.04	0.56
Range	0.28	0.83	0.60	0.74	0.70	2.21	0.24	0.09	4.90
Minimum	4.54	5.17	7.77	4.60	4.44	4.00	7.29	8.81	4.00
Maximum	4.82	6.00	8.37	5.34	5.14	6.21	7.53	8.90	8.90
Count	12	12	12	12	12	12	12	12	96
Confidence Level (95.0%)	0.055	0.140	0.130	0.124	0.130	0.403	0.049	0.016	0.340
%RSD	1.87	4.11	2.51	4.01	4.39	13	1.05	0.28	27

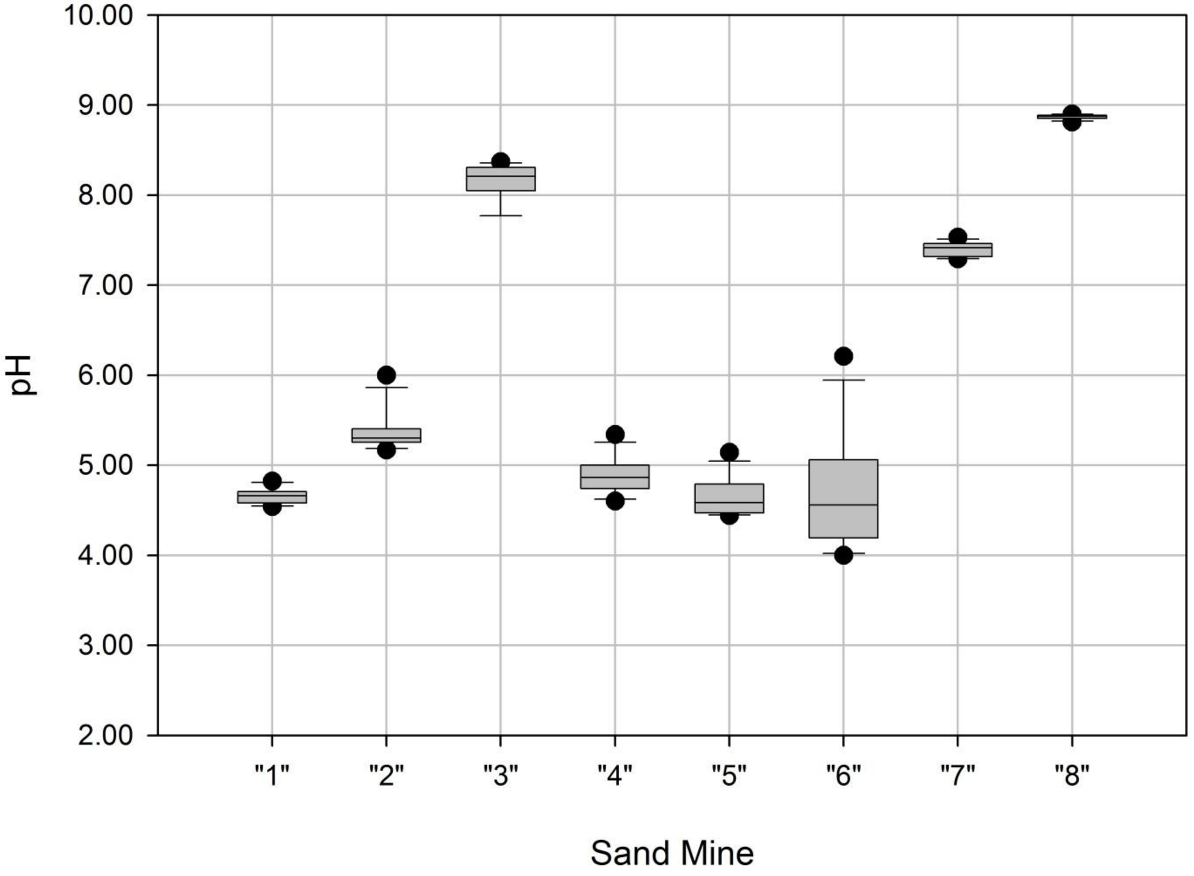


Figure 11-1. Box plots of soil pH by soil mine.

11.3.1.2 Operating characteristic (OC) curve for pH

For pH, the variance σ^2_{total} pooled across eight soils was 0.073 (Appendix D, Section D.1, Table D-1). The portion of this variance that was related to single-laboratory analytical testing was 0.0054 (Appendix B, Section B.9, Table B-34). The estimate of the variance component for multi-laboratory analytical testing was 0.0225 (Chapter 10, Section 10.5, Table 10-5, Material D). Thus, σ^2_{total} including single- and multi-laboratory analytical testing variances were 0.073 and 0.090, respectively, and the corresponding standard deviations or test errors were 0.27 and 0.30 pH units, respectively. In Figure 11-2 were plotted for pH and sample size $N = 3$ a series of OC curves at test errors σ of 0.20, 0.30, 0.40, and 0.50 pH units. Acceptance limits were pH 5 and pH 9 and critical (rejection) limits of pH 4 and pH 10 were assumed. Figure 11-2 suggested that for triplicate independent, randomly-selected samples with a normal pH distribution, the probability of accepting a good backfill (or power, 1-β) was 95% or better if test error was at or below 0.40 pH units; for a test error of 0.50 pH units, the power dropped to 81%. For $N = 2$, power was greater than 95% for a test error of 0.30 pH units but for a test error of 0.40 pH units dropped to 83%. As previously noted in Chapter 2 (Section 2.2.1), several options were available to improve the statistical power: (1) change the acceptance limits, (2) increase the number of samples, (3) reduce the test error, (4) shift more risk to the seller, (5) or modify the reinforcement design or material. Each and every one of these options has cost implications, but results from the inter-laboratory study suggested there was room to reduce the test error.

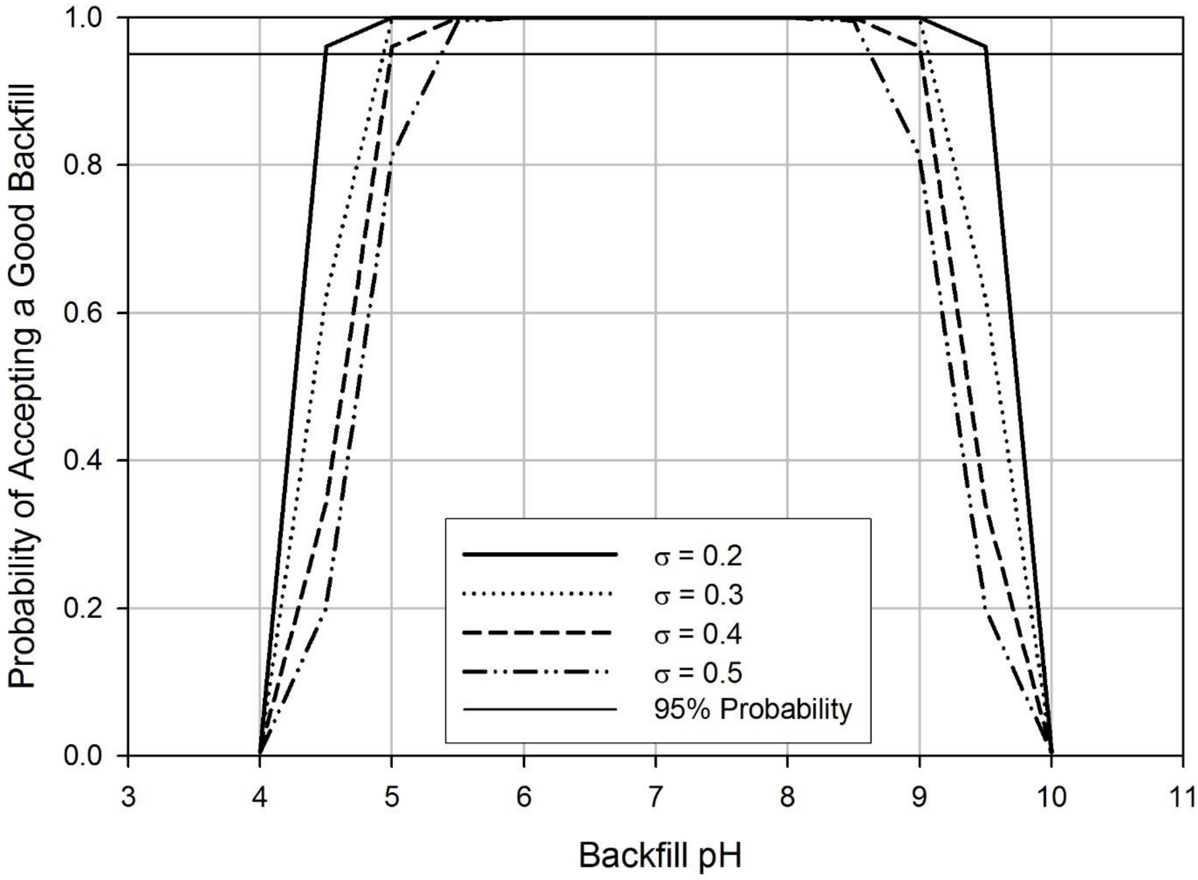


Figure 11-2. Operating characteristic (OC) curve for pH for sample size $N = 3$.

The difference in the means and variances between replicate and treatment studies suggested the relative influence of material mixing and subsampling at the source on the observed sample pH (Table 11-2). Note, for example, that for mine 6 the pH decreased from pH 4.70 to pH 4.39, and the latter pH failed to meet the lower acceptance limit for either metal and geosynthetic reinforcement. From Table 11-2 sample means were significantly different between replicate and treatment studies for soils from mines 3 and 4 and variances were significantly higher between replicate and treatment studies for soils from mines 5 and 6. In other words, for soil from mines 3 and 4, material handling between the mine and the laboratory affected the observed average pH; for mines 5 and 6, material handling between the mine and the laboratory diminished the observed variability in pH.

Table 11-2 Comparison of Replicate and Treatment Study Statistics for pH

Statistic	Mine Identifier							
	1	2	3	4	5	6	7	8
Replicate Average	4.66	5.37	8.15	4.88	4.65	4.70	7.40	8.87
Replicate Standard Deviation	0.09	0.22	0.20	0.20	0.20	0.63	0.08	0.03
Treatment Average	4.65	5.16	8.41	4.52	4.56	4.39	7.44	8.92
Treatment Standard Deviation	0.08	0.15	0.04	0.06	0.02	0.04	0.09	0.05
t-test (*p*)	0.81	0.11	0.00	0.00	0.18	0.12	0.52	0.19
F-test (*p*)	0.99	0.69	0.08	0.19	0.02	0.01	0.65	0.09

Elias et al. (2009) recommended that for an MSE wall six pH samples of sand be tested pre-construction and one pH sample be tested every 1,529 m^3 (2,000 yd^3, which is 100 to 200 truckloads, or ~70 lifts of 28 yd^3 per lift) during construction. Results for pH suggested that emphasis on pre-construction sampling was well-placed due to the potential lack of uniformity of source material with respect to pH. Recommendations to improve the buyer's statistical power were:

- Revise the FM for pH;
- Test at least three independent samples for pH per soil type, both pre-construction and post-emplacement;
- Provide operator training;
- Conduct routine on-site independent audits of the FM for pH (see Appendix G for an audit checklist); and
- Complete a Florida-wide inter-laboratory study of the revised FM within a year of its adoption.

11.3.2 FM for minimum resistivity

11.3.2.1 Distribution of minimum resistivity in mined soil

In Table 11-3 were presented the descriptive statistics and in Figure 11-3 the box plots for minimum resistivity of soil samples within and between samples collected from eight mines. For MSE wall backfill, soil minimum resistivity must be greater than 3,000 ohm-cm (Chapter 2, Section 2.1.2, Table 2-2). There was evidence—for both central tendencies (*t*-test, p = 0.00) and dispersion (*F*-test, $p = 0.00$)—that differences in sample processing and analysis between the first four and the last four mines affected minimum resistivity measurements within each soil (Figure 11-3). These differences were likely due to a change in the analytical procedure that preferentially measures the resistivity of the water rather than soil content in the soil slurry produced as water is added to the sample during testing. The minimum resistivity of replicates across mines 5 through 8 ranged from 9,500 to 64,000, with an average (± standard deviation) of 25,300 (± 11,700), and at the 95% confidence level, the average minimum resistivity was between 22,000 and 28,600. A single-factor ANOVA (Appendix D, Section D.2, Table D-2) revealed that the variability of minimum resistivity was greater between than within soils ($p = 0.00$); the hypothesis that the minimum resistivity averages were equal across soils from mines 5 through 8 was rejected. The hypothesis that the distribution of replicate minimum resistivity measurements was normal was not rejected for soil from all mines except mines 3 and 6; the hypothesis that the distribution of replicate minimum resistivity measurements was uniform was not rejected for soil from all mines except mines 3, 6, and 8.

Table 11-3 Descriptive Statistics for Minimum Resistivity

Statistic	Mines								
	1	2	3	4	5	6	7	8	Mines 5 - 8
Mean	57,600	135,000	8,780	152,000	19,100	36,400	33,000	12,500	25,300
Standard Error	7,470	5,380	1,110	22,300	1,820	2,950	1,040	441	1,690
Median	55,500	143,000	8,250	110,000	18,500	33,300	32,800	12,500	27,300
Mode	none	150,000	4,100	110,000	20,000	none	30,000	13,000	13,000
Std Dev	25,900	18,600	3,840	77,400	6,300	10,200	3600	1530	11,700
Sample Variance	6.69 E+08	3.48 E+08	1.48 E+07	5.98 E+09	3.96 E+07	1.05 E+08	1.30 E+07	2.34 E+06	1.37 E+08
Kurtosis	0.26	0.67	-0.85	0.99	7.74	4.72	-0.22	0.15	0.74
Skewness	1.01	-1.13	0.45	1.41	2.54	1.98	0.88	-0.19	0.73
Range	80,500	61,000	11,900	248,000	24,500	38,000	10,500	5,500	54,500
Minimum	29,500	94,000	4,100	77,000	13,000	26,000	29,500	9,500	9,500
Maximum	110,000	155,000	16,000	325,000	37,500	64,000	40,000	15,000	64,000
Count	12	12	12	12	12	12	12	12	48
Confidence Level (95.0%)	16,400	11,800	2,440	49,000	4,000	6,500	2,290	972	3,310
%RSD	45	14	44	51	33	28	11	12	46

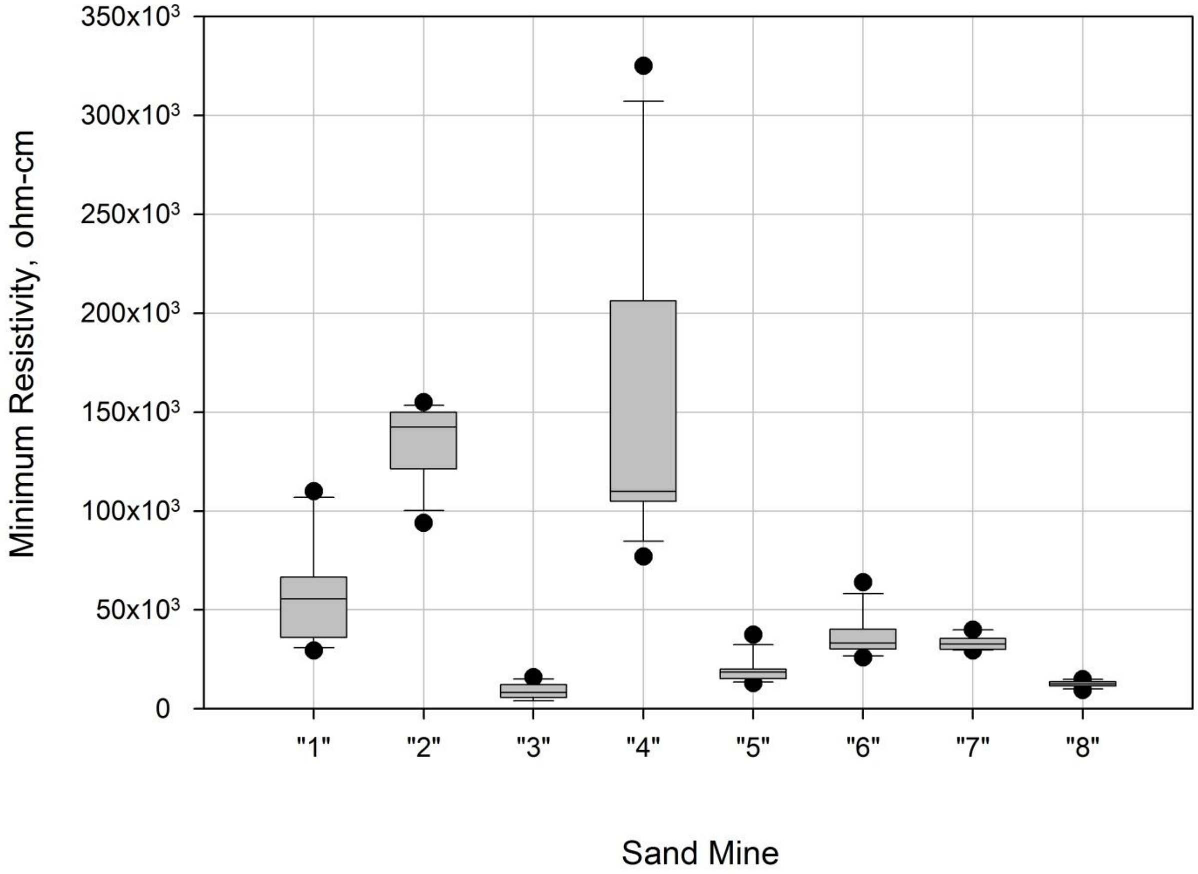


Figure 11-3. Box plots of soil minimum resistivity by soil mine.

11.3.2.2 Operating characteristic (OC) curve for minimum resistivity

Soil resistivity was measured with scaled meter readings, for example, from 100 to 1,000 ohm-cm, 1,000 to 10,000 ohm-cm, and 10,000 to 100,000 ohm-cm; the standard deviation of the measurement followed the scale and method precision across the scales was better described by a relative standard deviation (%RSD). For minimum resistivity, the variance σ^2_{total} pooled across eight soils and expressed as a squared relative standard deviation was 0.062 (Appendix D, Section D-2, Table D-2). The portion of this that was related to single-laboratory analytical testing was 0.00071 (Appendix B, Section B.9, Table B-36) and the multi-laboratory contribution was 0.035 (Chapter 10, Section 10.4, Table 10-1, Material B). Thus, σ^2_{total} including single- and multi-laboratory analytical testing squared relative standard deviations were 0.062 and 0.096, respectively, or %RSDs of 24.9% and 31.0%, respectively. In Figure 11-4 were plotted for minimum resistivity and for $N = 2$ a series of OC curves with test errors σ of 300, 600, 900, and 1200 ohm-cm or 10%, 20%, 30%, and 40% of the acceptance limit of 3,000 ohm-cm. A rejection limit of 1,000 ohm-cm was assumed (Chapter 2, Section 2.2.1). Section

Figure 11-4 suggested that for duplicate independent and random samples, the probability of accepting a good backfill (or power, 1-β) at 3000 ohm-cm was 95% or better if method reproducibility was at or below 600 ohm-cm (20%); for a method reproducibility of 900 ohm-cm (30%), the power dropped to 79%.

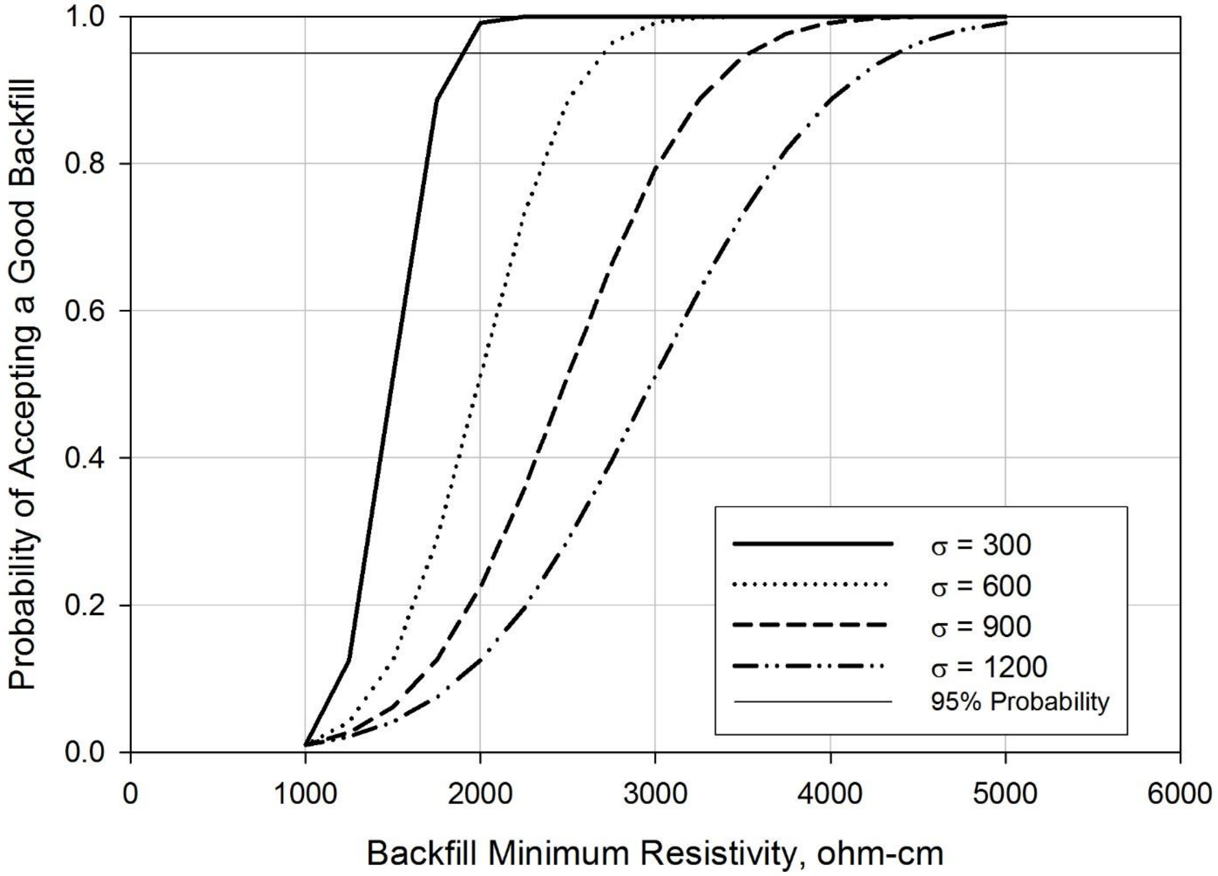


Figure 11-4. Operating characteristic (OC) curve for minimum resistivity for sample size N = 2.

As noted in Chapter 2 (Section 2.2.1), several options were available to improve the statistical power: (1) change the acceptance limits, (2) increase the number of samples, (3) reduce the test error, (4) shift more risk to the seller, (5) or modify the reinforcement design or material. Each and every one of these options has cost implications, but from the results of the inter-laboratory study there was room to reduce the test error; another possibility was to increase the acceptance limit for minimum resistivity to 4,000 ohm-cm. In doing so, for sample size $N = 2$ and $\sigma = 900$, the power was 99%.

The difference in the means and variances between replicate and treatment studies suggested an influence of material mixing and subsampling at the source on the observed sample minimum resistivity (Table 11-4). Note, for example, that for mine 7 the average minimum resistivity decreased 18% from 33,300 in the replicate study to 27,300 in the treatment study. From Table 11-4 the sample mean was significantly different between replicate and treatment studies for soils from mines 7 and 8 and variances were significantly higher between replicate and treatment studies for soils from mines 5 and 6. In other words, for soils from mine 7 and 8, material handling between the mine and the laboratory affected the observed average minimum resistivity; for mines 5 and 6, material handling between the mine and the laboratory diminished the observed variability in minimum resistivity.

Table 11-4 Comparison of Replicate and Treatment Study Statistics for Minimum Resistivity

Statistic	Mine Identifier			
	5	6	7	8
Replicate Average	19,100	36,400	33,300	12,500
Replicate Standard Deviation	6,300	10,200	3,600	1,530
Treatment Average	17,300	31,300	27,300	10,800
Treatment Standard Deviation	289	764	764	289
t-test (*p*)	0.36	0.12	0.00	0.00
F-test (*p*)	0.00	0.01	0.09	0.07

Elias et al. (2009) recommended that for an MSE wall three resistivity samples of sand be tested pre-construction and one resistivity sample be tested every 3,058 m^3 (4,000 yd^3, which is ~200 truckloads, or ~140 lifts of 28 yd^3 per lift) during construction. Results suggested that emphasis on pre-construction sampling was well-placed due to the potential lack of uniformity of source material with respect to minimum resistivity. Recommendations to improve the buyer’s statistical power were:

- Revise the FM for minimum resistivity;
- Increase the minimum resistivity acceptance limit to 4,000 ohm-cm;
- Test at least two independent samples for minimum resistivity per soil type, both pre-construction and post-emplacement;
- Provide operator training;
- Conduct routine on-site independent audits of the FM for minimum resistivity (see Appendix G for an audit checklist); and

- Complete a Florida-wide inter-laboratory study of the revised FM within a year of its adoption.

11.3.3 FM for chloride

11.3.3.1 Distribution of chloride in mined soil

Soil chloride concentrations were below the stated method detection level for soil samples from all eight mines.

11.3.3.2 Operating characteristic (OC) curve for chloride

For chloride, an inter-laboratory study yielded an estimate of 12 ppm for method reproducibility (Chapter 10, Section 10.4, Table 10-1), although this estimate did not include contributions from soil sampling or processing (Chapter 2, Section 2.2.3). The method reproducibility estimate was for an average soil concentration of 66 ppm and did not extend to higher chloride concentrations where further dilution of the soil extract compounded the error. An OC curve for chloride was built assuming a sample size $N = 1$ and test errors of 20, 40, 60, and 100 ppm (Figure 11-5). With a soil chloride concentration rejection limit of 500 ppm and acceptance limit of 100 ppm (Chapter 2, Section 2.2.1), a test error or method reproducibility could be as high 100 ppm and the probability of accepting a good backfill would still exceed 95%.

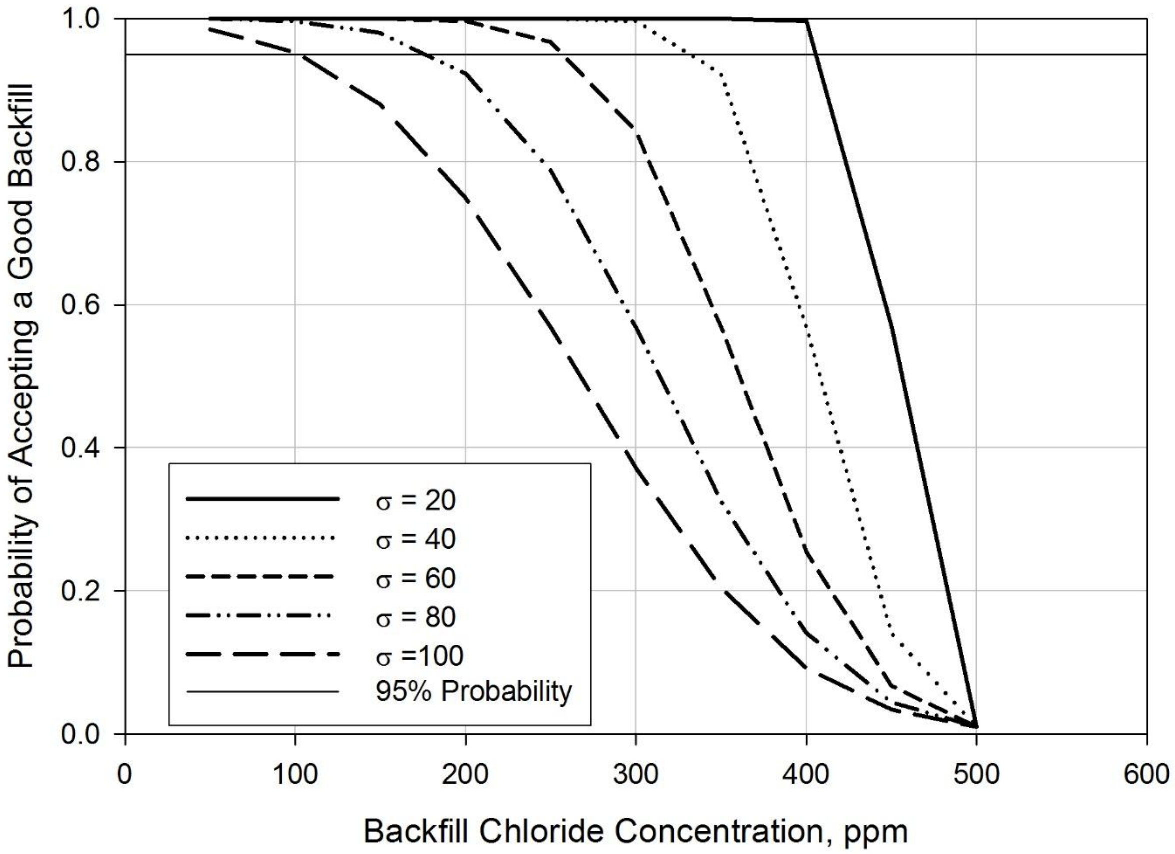


Figure 11-5. Operating characteristic (OC) curve for chloride for sample size $N = 1$.

No changes were recommended for the chloride concentration acceptance limit or the sample size based on the OC curve (Figure 11-5). Moreover, since minimum resistivity is a measure of dissolved salts concentration, a minimum resistivity exists above which the chloride concentration will be below 100 ppm. At a solution temperature of 25°C, for example, a 165-ppm sodium chloride (100-ppm chloride) solution has a calculated resistivity of 2,900 ohm-cm (Lide, 2001). The constituency of dissolved salts in a soil solution is more complex and the resistivity less predictable than for pure solutions but it may be possible to over time to establish a relationship between soil minimum resistivity and chloride concentration and from this determine if a test for soil chloride concentration were necessary. Recommended was an analysis of the minimum resistivity versus chloride concentration for soils across Florida after a two-year period of data collection under the revised Florida methods.

11.3.4 FM for sulfate

11.3.4.1 Distribution of sulfate in mined soil

Of the samples collected from eight mines, samples from only four mines had sulfate concentrations above the method's stated detection level. In Table 11-5 were presented the descriptive statistics and in Figure 11-6 the box plots for sulfate concentrations within and between samples collected from these four mines. For MSE wall backfill, soil sulfate concentration must be less than 200 ppm (Chapter 2, Section 2.1.2, Table 2-2). A single-factor ANOVA revealed that the variability of soil sulfate concentration was greater between than within soils ($p = 0.00$) (Appendix D, D.3, Table D-3) and the hypothesis that sulfate concentration averages were equal across the eight soils was rejected. Between samples from mines 1 and 3 and samples from mines 5 and 6, there was no evidence of a shift in sulfate results for central tendencies (*t*-test, $p = 0.22$) but there was a discernible shift in dispersion (*F*-test, $p = 0.00$), driven by the large dispersion seen for Youngquist sand from mine 3. Results from ruggedness studies for sulfate (Chapter 8, Section 8.3.4) and treatment studies for sulfate (Chapter 9, Section 9.1.5) do hint that precision was improved for drying at a lower temperature. Soil sulfate concentrations of replicates across mines 1, 3, 5, and 6 ranged from 0 to 102 ppm, with an average (± standard deviation) of 20 (± 18) ppm, and at the 95% confidence level the average sulfate concentration was between 15 and 25 ppm. The mean (average), median, and mode (if present) sulfate concentration from samples of soils from mines 1, 3, 5 and 6 were well below 200 ppm. Sulfate concentration standard deviations ranged from 4 to 30 ppm. Kurtosis (peakedness) and skewness of the distributions is significant when these values exceed ± 2.0, for example, but no distributions had significant kurtosis or skewness. The hypothesis that the distribution of replicate sulfate measurements was normal was not rejected for soil from all four mines except mine 6; the hypothesis that the distribution of replicate sulfate measurements was uniform was not rejected for soil from all four mines.

Table 11-5 Descriptive Statistics for Soil Sulfate Concentration

Statistic	Mine Identifier				
	1	3	5	6	All
Mean	13	34	24	10	20
Standard Error	2	9	1	1	3
Median	11	29	24	9	15
Mode	9	0	21	9	9
Standard Deviation	6	30	4	4	18
Sample Variance	39	917	16	15	324
Kurtosis	0.23	0.90	0.92	0.03	9
Skewness	0.74	0.99	0.80	-0.56	3
Range	21	102	15	12	102
Minimum	3	0	18	3	0
Maximum	24	102	33	15	102
Count	12	12	12	12	48
Confidence Level (95.0%)	4	19	3	2	5
%RSD	49	90	17	40	90

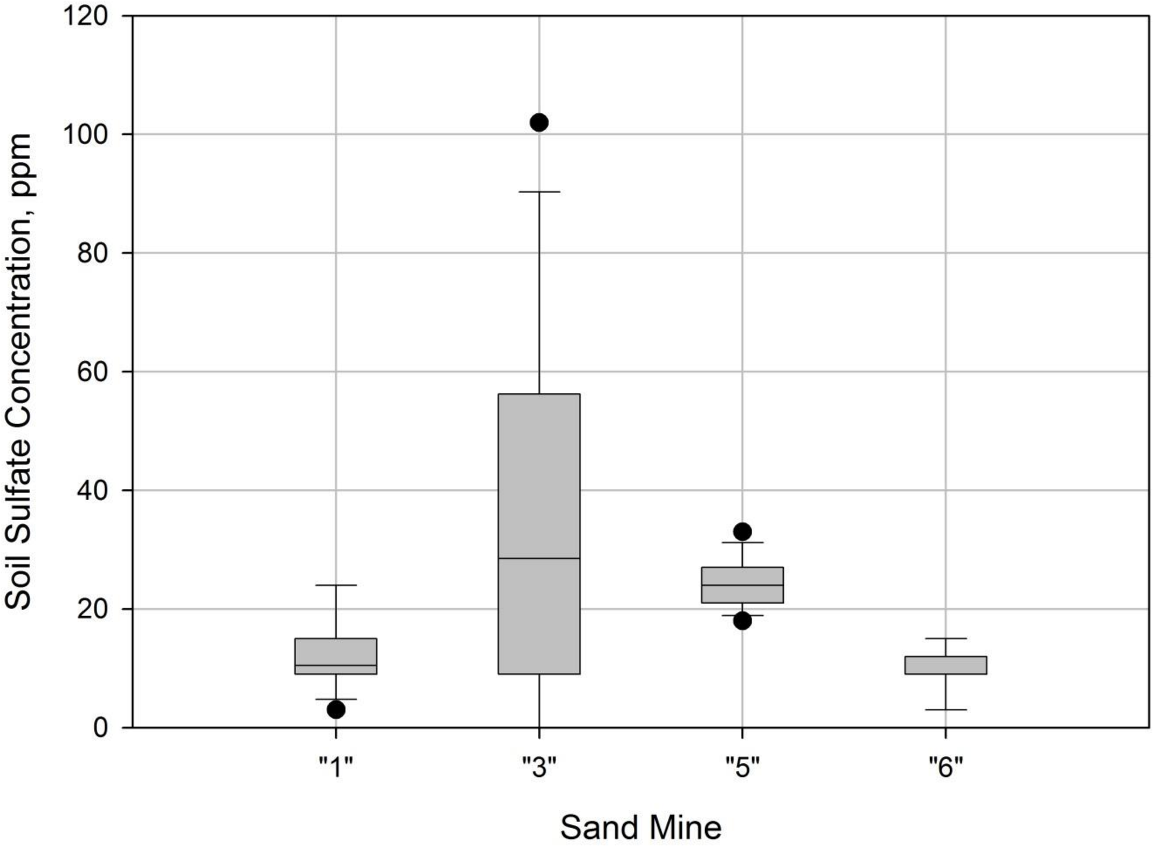


Figure 11-6. Box plots of soil sulfate concentration by soil mine.

11.3.4.2 Operating characteristic (OC) curve for sulfate

For soil sulfate, the σ_{total}^2 pooled across four soils was 247 (Appendix D, Section D.3, Table D-3). The portion of this variance that was related to single-laboratory analytical testing was 10 (Appendix B, Section B.9.3, Table B-38). The estimate of multi-laboratory variance was 242 (Chapter 10, Section 10.4, Table 10-1, Material B). Thus, σ_{total}^2 including single- and multi-laboratory analytical testing variances were 247 and 479, respectively, or corresponding standard deviations were 16 ppm and 22 ppm, respectively. In Figure 11-7 were plotted for sample size $N = 1$ a series of OC curves for sulfate and test errors σ of 20, 40, 60, 80 and 100 ppm. With a soil sulfate concentration rejection limit of 1,000 ppm and acceptance limit of 200 ppm, the probability of accepting a good backfill still exceeded 95% (curve not shown) for a test error as high 200 ppm.

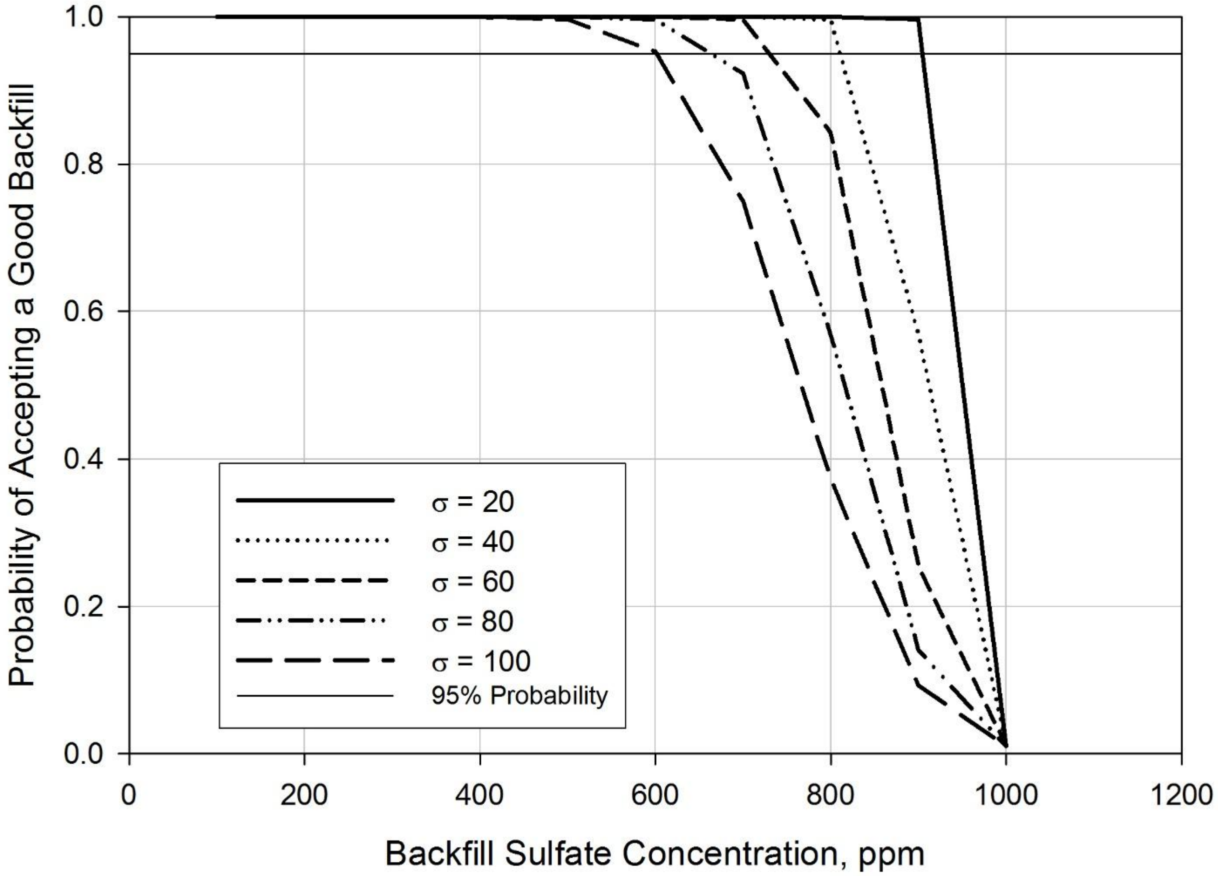


Figure 11-7. Operating characteristic (OC) curve for sulfate for sample size $N = 1$.

The difference in the means and variances between replicate and treatment studies suggested an influence of material mixing and subsampling at the source on the observed sample sulfate concentration (Table 11-6). Note, for example, that for mine 3 sulfate concentration was 5 ppm higher for the treatment study than for the replicate study. From Table 11-6 sample means were significantly different between replicate and treatment studies for none of the soils tested but variance was significantly higher between replicate and treatment studies for soils from mine 6. In other words, for soil from 6, material handling between the mine and the laboratory diminished the observed variability in sulfate concentration.

Table 11-6 Comparison of Replicate and Treatment Study Statistics for Sulfate

Statistic	Mine Identifier			
	1	3	5	6
Replicate Average	13	34	24	10
Replicate Std Deviation	6	30	4	4
Treatment Average	10	39	24	12
Treatment Std Deviation	2	5	3	0
t-test (p)	0.21	0.58	1.00	0.07
F-test (p)	0.14	0.06	0.82	0

No changes were recommended for the sulfate concentration acceptance limit or the sample size based on the OC curve (Figure 11-7). Moreover, since minimum resistivity represents a measure of dissolved salts concentration, a minimum resistivity exists above which the sulfate concentration will be below 200 ppm. At a solution temperature of 25 ^{o}C, for example, a 445-ppm sodium sulfate (200-ppm sulfate) solution has a calculated resistivity of 1,380 ohm-cm (Lide, 2001), for example. The constituency of dissolved salts in a soil solution is more complex and the resistivity less predictable than for pure solutions but it may be possible to over time to establish a relationship between soil minimum resistivity and sulfate concentration and from this determine if a test for soil sulfate concentration were necessary. Recommended was an analysis of the minimum resistivity versus sulfate concentration for soils across Florida after a two-year data collection period under the revised Florida methods.

11.4 Summary

The statistical approach taken to estimate the appropriate number of samples for pre-construction and post-emplacement testing assumed that independent, randomly-selected samples of soil were collected and that soil pH, minimum resistivity, chloride, or sulfate concentrations were normally distributed. Sampling, however, was subject to selection bias because of the practical limits on geographical coverage, pre-selected characteristics of the soil, and accessibility of soil in stockpiles or soil strata in pits, and the results reported herein are not fully representative of Florida's resources. Chloride concentrations in soils from all eight mines were below the stated method detection level of 15 ppm. For pH, minimum resistivity, and sulfate concentrations, data distributions were in general not different from normal but they were also in general not different from uniform, a likely consequence of the limited number of replicates tested. Reported soil sample variances included contributions from the material, sampling, processing, environment and analysis, where analysis was accomplished by USF soils laboratory. These variances were adjusted by subtracting single-laboratory contributions based on treatment studies and adding multi-laboratory contributions from the inter-laboratory study to obtain an estimate of the total test error $\sqrt{\sigma_{total}^2}$ for the method. Operating characteristic (OC) curves were developed for each method and for a range of test errors, inclusive of the estimated total test error.

Based on the method OC curves, QA plan recommendations were as follows:

- For pH, revise the FM, test at least three independent samples for pH per soil type both pre-construction and post-emplacement; provide operator training and routine on-site laboratory audits of the FM (see Appendix G for an audit checklist); and conduct a Florida-wide inter-laboratory study of the revised FM within a year of its adoption.

- For minimum resistivity, revise the FM, test at least two independent samples per soil type for minimum resistivity both pre-construction and post-emplacement; impose a higher acceptance limit for minimum resistivity of 4000 ohm-cm; provide operator training and routine on-site laboratory audits of the FM (see Appendix G for an audit checklist); and conduct a Florida-wide inter-laboratory study of the revised FM within a year of its adoption.

- For chloride and sulfate, revise the FM, test at least one independent sample per soil type both pre-construction and post-emplacement, and investigate the relationship between minimum resistivity versus chloride and sulfate concentrations for soils across Florida after a two-year data collection period under the revised Florida methods to see if further testing of chloride and sulfate were necessary for select backfill.

12 Geochemical Modeling of Ion Transport in Sandy Soil

12.1 Problem Statement

Investigated through geochemical modeling was the hypothesis that soil mined from the subsurface and placed on the surface either in a stockpile or as backfill in an MSE wall over time undergoes a change in corrosion properties due to biological, chemical, or physical processes induced by infiltrating rainfall. The goals of this analytical modeling effort were (1) to recommend changes to the QA plan for corrosion AQC, if any, and (2) to assess the need for more in-depth modeling supported by field and laboratory measurements that were beyond the scope of this project. PHREEQC—pH redox equilibrium in C language—version 3 was chosen for the modeling effort.

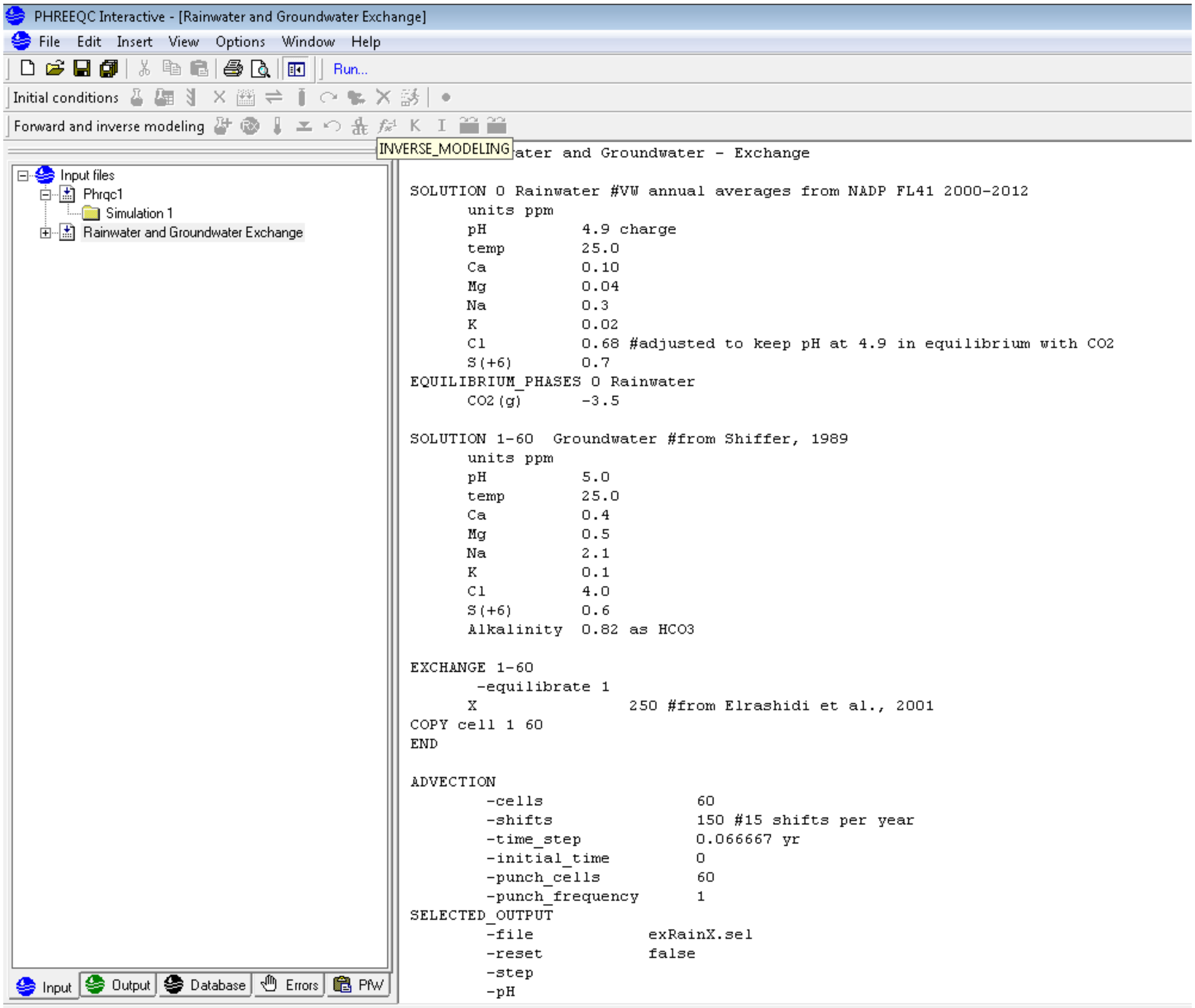
12.2 Model Description

PHREEQC v 3 was a publicly-available model maintained by the U. S. Geological Survey (USGS) and was available for download at http://wwwbrr.cr.usgs.gov/projects /GWC_coupled/phreeqc/. PHREEQC v 3 was "a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations" and included a large and expandable database of multi-phase equilibria and related dependencies for chemical reactions of importance in groundwater, rainwater, seawater, soil water, and surface water (Parkhurst and Appelo, 2013). Example input and output files were provided with the model download, which supplemented a User's Manual for the model (Parkhurst and Appelo, 2013). Published model applications such as clean-up of nuclear contamination and acid mine drainage (Hormann and Kirchner, 2002), drinking water treatment (Rozell, 2010), subsurface nutrient transport (Domagalski and Johnson, 2011), soil profiling (Appelo,1994), and concrete leaching (Schiopu et al., 2009) gave a sense of the model's broad capabilities.

The PHREEQC input files were created and output files reviewed from a user-friendly interface (Figure 12-1); also available at this interface were error files, databases, example files, and a glossary of code words. Program operations were directed through a sequence of key words and data. Program operations used for this modeling effort included (1) initial solution or speciation, (2) initial exchange, and (3) advection calculations, in that order. Reaction temperatures were set to 25 ^{o}C. For equilibrium calculations, units for input species were converted to moles/liter and the moles of each species were distributed between all phases and exchange sites according to databased reactions and partitioning coefficients (Table 12-1) (Parkhurst and Appelo, 2013). In addition to cation exchange, the model was run with the groundwater and infiltrating rainwater in equilibrium with carbon dioxide and quartz. Quartz was assumed to be abundant. For cation exchange, groundwater was equilibrated with soil exchanger X, based on the soil's cation exchange capacity (CEC); the exchanger's composition changed but not the groundwater composition. PHREEQC uses by default a Gaines-Thomas method, where the activities of the equivalent fractions (as opposed to the mole fractions) were used. Equations 12-1 and 12-2 shows the exchange were a multivalent ion replaces a monovalent ion. The databased partitioning coefficients were $Na^+ + X^- \leftrightarrow NaX$, log K = 0.0; $K^+ + X^- \leftrightarrow KX$; log K = 0.7; $Ca^{+2} + 2X^- \leftrightarrow CaX_2$, log K = 0.8; $Mg^{+2} + 2X^- \leftrightarrow MgX_2$, log K = 0.6. The hydronium ion (H^+) was not included in the cation exchange. According to Bohn et al. (1985), in acid soils exchangeable aluminum can be present and appears as exchangeable H^+ when salt is added to displace the adsorbed cations; otherwise exchangeable H^+ can occur in soils with pH < 4.

$$A^{2+} + BX \leftrightarrow 0.5AX_2 + B^+ \tag{12-1}$$

$$K_{A/B} = \frac{\{AX_2\}^{0.5}}{\{BX\}} \frac{\{B^+\}}{\{A^{2+}\}^{0.5}} \tag{12-2}$$



```
ater and Groundwater - Exchange

SOLUTION 0 Rainwater #VW annual averages from NADP FL41 2000-2012
      units ppm
      pH          4.9 charge
      temp        25.0
      Ca          0.10
      Mg          0.04
      Na          0.3
      K           0.02
      Cl          0.68 #adjusted to keep pH at 4.9 in equilibrium with CO2
      S(+6)       0.7
EQUILIBRIUM_PHASES 0 Rainwater
      CO2(g)      -3.5

SOLUTION 1-60  Groundwater #from Shiffer, 1989
      units ppm
      pH          5.0
      temp        25.0
      Ca          0.4
      Mg          0.5
      Na          2.1
      K           0.1
      Cl          4.0
      S(+6)       0.6
      Alkalinity  0.82 as HCO3

EXCHANGE 1-60
       -equilibrate 1
      X                250 #from Elrashidi et al., 2001
COPY cell 1 60
END

ADVECTION
        -cells                  60
        -shifts                 150 #15 shifts per year
        -time_step              0.066667 yr
        -initial_time           0
        -punch_cells            60
        -punch_frequency        1
SELECTED_OUTPUT
        -file             exRainX.sel
        -reset            false
        -step
        -pH
```

Figure 12-1 User's input screen for PHREEQC.

Table 12-1 Selected Aqueous-Phase or Precipitation Reactions

Aqueous-Phase or Precipitation Reactions	Log K	Dissolved Ions, Minerals and Gases (g)
$Ca^{+2} + H_2O \leftrightarrow CaOH^{+} + H^{+}$	-12.8	aqueous
$Ca^{+2} + CO_3^{-2} \leftrightarrow CaCO_3$	3.22	aqueous
$Ca^{+2} + CO_3^{-2} + H^{+} \leftrightarrow CaHCO_3^{+}$	11.4	aqueous
Ca+2 + HSO4- $\leftrightarrow$ CaHSO4+	1.08	aqueous
$CaCO_3 \leftrightarrow CO_3^{-2} + Ca^{+2}$	-8.34	aragonite
$CaCO_3 \leftrightarrow CO_3^{-2} + Ca^{+2}$	-8.48	calcite
$CaMg(CO_3)^2 \leftrightarrow Ca^{+2} + Mg^{+2} + 2\ CO_3^{-2}$	-17.0	dolomite
$Ca^{+2} + SO_4^{-2} \leftrightarrow CaSO_4$	2.25	aqueous
$CaSO_4 \leftrightarrow Ca^{+2} + SO_4^{-2}$	-4.28	anhydrite
$CaSO_4{:}2H_2O \leftrightarrow Ca^{+2} + SO_4^{-2} + 2\ H_2O$	-4.58	gypsum
$CO_2 \leftrightarrow CO_2$	-1.46	CO2(g)
$CO_3^{-2} + H^{+} \leftrightarrow HCO_3^{-}$	10.3	aqueous
$CO_3^{-2} + 2\ H^{+} \leftrightarrow CO_2 + H_2O$	16.7	aqueous
$H_2 \leftrightarrow H_2$	-3.10	H_2(g)
$2\ H^{+} + 2\ e^{-} \leftrightarrow H_2$	-3.15	aqueous
$H_2O \leftrightarrow OH^{-} + H^{+}$	-14.0	aqueous
$H_2O \leftrightarrow H_2O$	1.50	H_2O(g)
$2\ H_2O \leftrightarrow O_2 + 4\ H^{+} + 4\ e^{-}$	-86.1	aqueous
$KCl \leftrightarrow K^{+} + Cl^{-}$	0.90	sylvite
$K^{+} + SO_4^{-2} \leftrightarrow KSO_4^{-}$	0.85	aqueous
$Mg^{+2} + H^{+} + CO_3^{-2} \leftrightarrow MgHCO_3^{+}$	11.4	aqueous
$Mg^{+2} + H_2O \leftrightarrow MgOH^{+} + H^{+}$	-11.4	aqueous
$Mg^{+2} + CO_3^{-2} \leftrightarrow MgCO_3$	2.98	aqueous
$Mg^{+2} + SO_4^{-2} \leftrightarrow MgSO_4$	2.37	aqueous
$Na^{+} + CO_3^{-2} \leftrightarrow NaCO_3^{-}$	1.27	aqueous
$NaCl \leftrightarrow Cl^{-} + Na^{+}$	1.57	halite
$Na^{+} + HCO_3^{-} \leftrightarrow NaHCO_3$	-0.25	aqueous
$Na^{+} + SO_4^{-2} \leftrightarrow NaSO_4^{-}$	0.70	aqueous
$O_2 \leftrightarrow O_2$	-2.89	O_2(g)
$SiO_2 + 2\ H_2O \leftrightarrow H_4SiO_4$	-2.71	SiO_2(a)
$SiO_2 + 2\ H_2O \leftrightarrow H_4SiO_4$	-3.55	chalcedony
$SiO_2 + 2\ H_2O \leftrightarrow H_4SiO_4$	-3.98	quartz
$SO_4^{-2} + H^{+} \leftrightarrow HSO_4^{-}$	1.99	aqueous

Transport by advection was modeled without dispersion or diffusion, which simulated plug flow. A theoretical soil column was divided into adjacent cells and the fluid in each cell was initialized to that of groundwater in equilibrium with carbon dioxide, quartz, and exchanger *X*. The infiltrating rainfall was ‘shifted’ from cell 0 to cell 1 at the first time step; simultaneously, the groundwater in cell 1 was shifted to cell 2, and so forth. At each time step, the fluids moved another step down the column. Once in a new cell, the fluid was equilibrated with carbon dioxide, quartz, and exchanger *X*.

12.3 Model Inputs and Parameters

For 1-D transport modeling in PHREEQC, soil with isotropic properties was assumed to be in the form of a column with dimensions of 6 m x 6 m x 6 m = 216 m^3, and to have an available pore volume of 30%. Flow of rainwater was assumed to be vertical and downward through the column. To model unsaturated flow, the column was sliced horizontally into 60 equal cells, such that each cell was water-saturated during a weekly rainfall event of 30-mm (1.2 in) or greater, which was assumed to happen 15 times per yr based on the probabilities in Figure 12-2 (NADP, 2015). Thus, the total pore volume in the column was 0.030 m x 6 m x 6 m = 1.08 m^3 x 60 cells = 64.8 m^3, and with a time step or 'shift' of 1/15 yr, one column's pore volume was exchanged in 60 shifts or 4 years.

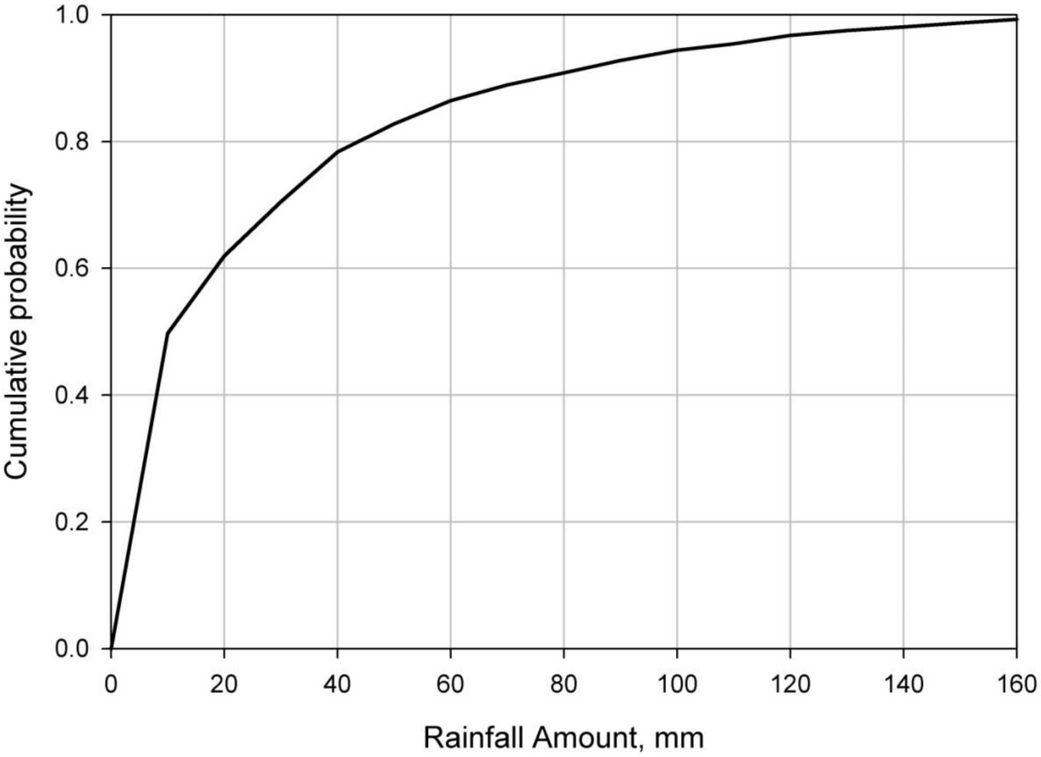


Figure 12-2. Cumulative probability for weekly rainfall amount at NADP's FL41 site in Sarasota County (2000 through 2012).

For rainwater, annual average precipitation-weighted concentrations for major ions were downloaded from the National Atmospheric Deposition Program (NADP) website for a National

Trends Network (NTN) site FL-41 in Sarasota County (NADP, 2015), and these concentrations were averaged over the years 2000 to 2012 (Table 12-2). Note that the precipitation-weighted average concentrations were lower than the weekly median concentrations reported in Chapter 2, (Section 2.1.3, Table 2-5). The average rainfall amount was 1300 mm (940 mm to 1650 mm) and the electrical conductivity (EC) of rainwater was ~10 µS/cm. The nitrogen species—ammonium (NH_4^+) and nitrate (NO_3^-)—were not input and the chloride concentration was adjusted upward from 0.50 to 0.68 ppm to maintain a charge balance. Groundwater median ionic composition was based on 11 samples collected from surficial aquifer wells in Ocala National Forest (Schiffer, 1989). The EC and alkalinity of groundwater were 27 µS/cm at 25°C and 0.82 ppm, respectively (Schiffer, 1989).

Table 12-2 Modeled ionic composition of rainwater and groundwater

Source	pH Lab	Units are ppm					
		Ca^{++}	Cl^-	K^+	Mg^{++}	Na^+	$SO_4^=$
Rainwater	4.9	0.1	0.5	0.02	0.04	0.3	0.7
Groundwater	5.0	0.4	4	0.1	0.5	2.1	0.6
Source	pH Lab	Units are moles/liter					
		Ca^{++}	Cl^-	K^+	Mg^{++}	Na^+	$SO_4^=$
Rainwater	4.9	2.50E-6	1.92E-5	5.12E-7	1.65E-6	1.31E-5	7.29E-6
Groundwater	5.0	9.98E-6	1.13E-4	2.56E-6	2.06E-5	9.14E-5	6.25E-6

Soil properties were based on Candler soil, an uncoated hyperthermic Typic Quartzipsamments, which is a permeable, well-drained sandy soil present in central Florida in thick deposits, and one of the Lake series soils based on a classification by the U. S. Department of Agriculture (Table 12-3). Candler soil pH, % organic matter (%OM), cation exchange capacity (CEC), and EC were obtained from Elrashidi et al. (2001). Note the reasonable agreement between groundwater and soil pH and EC.

Table 12-3 Candler Soil Properties

Soil	pH	%OM	CEC, mol/kg	EC, µS/cm
Candler	5.05	0.65	0.0405	30

Each cell had a soil volume of $3.6\ m^3$ x 70% = $2.52\ m^3$ and with an assumed sand density of $2,500\ kg/m^3$, the mass of soil in each cell was 6,300 kg and the CEC per cell was 6,300 kg x 0.04 moles/kg ≅ 250 moles of exchange sites per cell. Perhaps the soil closest in composition to Candler soil was from Mine 2 in Haines City (nicknamed Jahna sand) with a pH of 5.16, a resistivity of 54,000 ohm-cm (19 µS/cm), and 0.08 %OM.

Refer to Appendix E for the PREEQC input and output files. Due to the file length, the output included some but not all of the cell equilibration results. Temporal values for pH, calcium, potassium, and sodium were printed to a separate file for plotting. Carbon dioxide concentration was initially adjusted such that the groundwater pH did not change much from the reported pH 5.0 during the equilibration step. In the simulation carbon dioxide equilibrated with groundwater at a partial pressure of ~12,000 ppm, which was in line with subsurface CO_2 concentrations reported and modeled by Macpherson (2009).

12.4 Model Results and Discussion

Modeled was a conservative case of rainwater and soil interaction, conservative in the sense that the groundwater/soil system modeled had a low buffering capacity and a pH already close to that of rainwater. In this simulation, at four yr the last cell shifted from properties of groundwater to properties of rainwater, where both were equilibrated with the exchange sites, with ~12,000-ppm carbon dioxide, and with quartz. Precipitation of solids including calcite, dolomite, gypsum, etc., listed in Table 12-1 was not predicted, but chalcedony (SiO_2) had a saturation index of -0.43, the closest of any of the solids to saturation. With rainwater infiltration, the soil exchange sites picked up calcium and let go potassium and chloride; moreover, the pore water pH decreased from 5.05 to 4.67 (Figure 12-3). (Modeled pore water pH decreases to below pH 5.00 even if soil column carbon dioxide concentration is assumed to equilibrate with the atmospheric concentration.) These results suggested that the possibility existed for well-leached, poorly buffered quartz-type sands to reach a new equilibrium with rainwater within a few years after emplacement in a stockpile or behind an MSE wall.

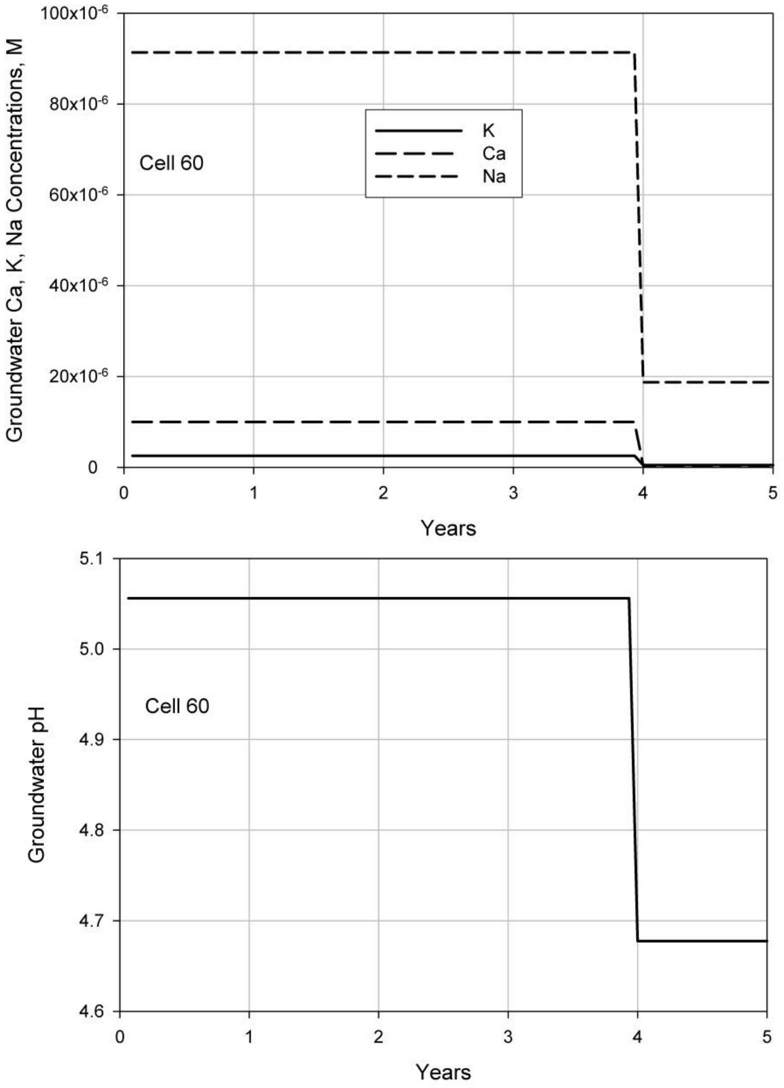


Figure 12-3. Modeled groundwater ion concentrations and pH at soil column exit.

12.5 Summary

Geochemical modeling with the USGS model PHREEQC for a conservative case of a low-ionic strength and poorly buffered sandy (quartz) backfill revealed that in a few years' time the pore water of stockpiled or emplaced backfill could equilibrate with infiltrating rainfall. The model results suggested that a soil's buffering capacity might be important consideration when metal is used as reinforcement in MSE wall backfill. Field and laboratory testing of candidate sands to calibrate the model were recommended ahead of any proposed changes to the QA plan based on model results.

13 Revised Florida Methods for pH, Resistivity, Chloride and Sulfate

13.1 Introduction

Results of field testing and laboratory analyses suggested that the accuracy and precision of the Florida Methods (FMs) for pH, minimum resistivity, chloride, and sulfate could be improved with relatively small changes in method procedures, as discussed in Sections 13.2 through 13.6. Proposed changes to the FMs fall into one of five categories: (1) minor edits to method grammar, organization, and units of measure; (2) updates to the apparatus and reagents sections, with a hazardous materials note as appropriate; (3) step-by-step instructions to facilitate method oversight; (4) one or more quality assurance/quality control procedures; and (5) a new section for method precision and bias. Revised FMs for pH, minimum resistivity, chloride, and sulfate are found in Appendix F. Note that the proposed changes were based on studies performed with select backfill and may not extend to water samples or to soil samples with a significant content of salt, clay or organic matter.

13.2 FM for pH

Changes to the scope, apparatus, reagent, samples, sample preparation, and test procedure sections of the FM were proposed as was the inclusion of a precision and bias section in the FM. Based on ruggedness and other factor analysis studies as well as laboratory visits (Chapters 6, 8, and 9) these major sources of variability were identified in the FM using a calibrated pH meter/electrode system:

- Condition of the electrode,
- Measurement temperature,
- Electrode memory effects, and
- Ionic strength of the soil solution.

The pH meter combination electrode is a delicate and sensitive sensor and with routine treatment and use its lifetime is ~18 months. A 3-in-1 combination electrode typically encases a glass-bulb indicating electrode, a silver/silver chloride reference electrode, and a thermocouple. Over time and with use the reference electrode is consumed, but temporary or permanent damage to the electrode can be caused by contamination or depletion of the filling solution, scratches or cracks on the glass bulb surface, and clogging of the liquid junction, as examples. Electrode condition can be monitored through calibration and performance checks. The revised method calls for a three-buffer (pH 4.00, 7.00, and 10.00) calibration, a calibration slope between 95% and 102% of theoretical, an offset of less than 10 mV, and a minimum 10-sec stable pH reading. Attention to electrode performance is critical to a precise and accurate pH measurement.

Measured pH is inversely proportional to temperature and pH meter/electrode systems are typically designed for a standard temperature of 25°C (Chapter 3, Section 3.2.1). A pH meter with automatic temperature compensation (ATC) measures and corrects for the sample temperature. Ideally, the buffers and the samples are 25°C, but with ATC, buffers and samples need be at or near the same temperature. The proposed revised method specified a pH/mV meter with ATC and equipped with a 3-in-1 combination electrode (Appendix F.1).

For pH measurement in low-ionic strength samples, the observed pH may be biased high because of the mismatch between the ionic strength of the calibration buffers and the sample and because of sample dilution. Select backfill, by virtue of its low fine particle content, low chloride and sulfate content, and high resistivity has relatively low ionic strength. According the pH meter/electrode sales literature (Bier, 2009; Thermo-Scientific, 2007), this bias can be reduced in three ways: (1) with use of low-ionic strength buffers, (2) with use of an electrode that has a high flow rate of electrolyte through its liquid junction, and (3) by increasing the ionic strength of the sample. The latter approach is the easiest way to reduce measurement bias in low-ionic strength water samples but causes a significant decrease in pH for soil samples, where the soil surface and pore water equilibria influence proton activity (refer to Chapter 9, Section 9.2.7, for further discussion).

Equilibration period and storage temperature were two other factors that had a significant effect on pH in ruggedness or treatment studies. For pH, a significant difference was seen between a ~0-min and a 30-min equilibration period but no significant difference between a 30-min and a 60-min equilibration period; therefore, a 30-min equilibration period was retained in the method. In the treatment studies with soils from mines 5-8, pH of samples stored in refrigerator and then warmed to room temperature were closest to the pH of samples measured on site. Therefore, instructions for cool transport and cold storage were retained in the method.

The electrode has a memory of its previous measurement and the contribution of this memory on the current pH measurement was more pronounced for low-ionic strength (low salt content) solutions. The memory effect on sample pH could be reduced by careful attention to rinsing and drying the electrode between measurements and by a second or even third consecutive measurement of sample pH.

For pH measurement in low-ionic strength solutions a stable pH reading could take 5 minutes or more to obtain, as the reading is affected by the exchange of carbon dioxide between the sample and the atmosphere, the effects of stirring and vibrations, and a mismatch between the ionic strength of the sample and the reference solution in the electrode. If after ~ 5 min the pH reading does not stabilize in a gently stirred sample, a pH reading in the unstirred sample should be recorded.

13.3 <u>FM for Minimum Resistivity</u>

Changes to the scope, apparatus, reagent, samples, sample preparation, and test procedure sections of the FM were proposed as well as the inclusion of a precision and bias section in the FM. Based on ruggedness and other factor analysis studies as well as laboratory visits (Chapters 6, 8, and 9), these major sources of variability were identified in the FM using a Nilsson Model 400 resistivity meter:

- Water content of soil slurry placed in the soil box during resistivity testing, and
- Measurement temperature.

The components of soil resistivity are soil liquids, solids, and voids (Chapter 3, Section 3.3.1). As the water content of a soil sample is increased beyond saturation, the path that ions must travel is increasingly free of impediment and soil resistivity drops until the soil is a dilute suspension in water. At the same time, the addition of deionized water dilutes the concentration of dissolved ions, which raises the resistivity. Minimum resistivity occurs at the intersection of these two effects. ASTM and AASHTO standards represented two different positions along the soil resistivity continuum: ASTM G187 measured soil resistivity when the soil is just saturated and AASHTO T288 measured minimum soil resistivity, with the water from soil slurry decanted into the soil box as the water content in the slurry increases. The FM for minimum resistivity did not provide direction on how to dispense soil slurry into the soil box, so this decision was left to the method operator. The proposed revised FM adopted the more conservative approach of AASHTO T288.

Resistivity measurements are sensitive to temperature (Chapter 3, Section 3.3.1); for example, resistivity can decrease by 10% if the measurement temperature is increased from 23°C to 28°C. Minimum resistivity measurements should be made at room temperature and the soil slurry temperature recorded during the measurement procedure in case temperature played a significant role in observed soil minimum resistivity between quality assurance, verification, and resolution samples.

A higher ion concentration in dilution water translates into a lower resistivity. Dilution water resistivity should be high enough not to contribute to or obscure the resistivity of the wetted soil, and ASTM D1193 Type 4 reagent water, which has a lower resistivity bound of 200,000 ohm-cm, was recommended. A routine check of dilution water as part of laboratory QA/QC was recommended because on-site water treatment systems can experience break-through of ions and bottled water—once opened—can over time absorb ions from acidic and basic gases in the atmosphere.

The resistivity meter calibration can be checked with one or more resistors that span the range of interest but a resistivity measurement of a conductivity standard will check not only the meter, but the lead connections, soil box, and measurement temperature. A resistivity meter calibration with a 250 µS/cm (4,000 ohm-cm) calibration standard at least once per quarter was proposed.

13.4 <u>FM for Chloride</u>

Changes to the scope, apparatus, reagents, samples, sample preparation, and test procedure sections of the FM were proposed, as well as the inclusion of a precision and bias section in the FM. The FM for chloride in soil and water is based on a silver nitrate titration of a sample that is amended with potassium chromate. Dissolved silver combines first with chloride and then with chromate in a mixture of the two. Both silver chloride and silver chromate are insoluble in water but silver chromate is a brown-red crystal and its appearance in the sample marks the titration endpoint. Hach chloride test kits (or equivalent) were recommended for laboratory-based screening of water and soil chloride concentrations; for a greater degree of accuracy and precision the analytical methods as described by the Standard Method for the Evaluation of Water and Wastewater (SMEWW) 4500-Cl^- or 4110 B for anions (Rice et al., 2012) were recommended. The SMEWW method 4500- Cl^- uses smaller increments of titrant and imposes additional QA/QC; SMEWW method 4110 B can detect lower anion concentrations but is not appropriate for seawater samples. Based on ruggedness and other factor analysis studies as well as laboratory visits (Chapter 6, 8, and 9), these major sources of variability in the FM were identified using the chloride test kit:

- Soil mass,
- Suspended solids or color in the filtered sample extract,
- Incorrect or out-of-date reagents, and
- Blank correction.

For chloride determination an accurate soil mass can be obtained if the soil is dried to a constant mass and its mass weighed on an analytical balance; these two requirements limit the portability of the method. In laboratory studies, suspended particles or color present in sample extracts interfered with the color change at the titration endpoint, with the effect that extra titrant was added and the chloride concentration in soil was thus biased high. Attempts to clarify filter extracts included ferric sulfate addition, a 1:1 water-to-soil ratio in the soil extraction, serial gravity filtration using Whatman 4 and Whatman 42 filters, centrifugation, and vacuum filtration through a membrane filter (Chapters 5, 9). One effective combination for clearing the sample extract was to add ~0.2 g of ferric sulfate dissolved in 1 mL of water to the sample extract, followed by at least three hr of settling time, gravity filtration through a Whatman 41 filter, and finally vacuum filtration through a 0.45-micron filter. Vacuum filtration through a 0.45-micron membrane filter was recommended as a final filtration step. Also recommended were separate 3:1 water-to-soil extracts for chloride and sulfate, so that ferric sulfate could be added directly to the unfiltered extract, if needed. If ferric sulfate were not needed, only one extract has to be filtered for chloride and sulfate determinations. A chloride check standard and an associated reagent blank were included in the proposed revised FM to help establish the sample color at the titration endpoint, to guard against bad reagents, and to subtract out any chloride contamination in the dilution water.

13.5 FM for Sulfate

Changes to the scope, apparatus, reagents, samples, sample preparation, and test procedure sections of the FM were proposed, as well as the inclusion of a precision and bias section in the FM. The FM for sulfate in soil and water in based on the reaction of water-dissolved sulfate and barium to form an insoluble precipitate of barium sulfate. The turbidity produced by this precipitate is proportional to the sulfate concentration in the sample. The Hach sulfate photometer test kit (or equivalent) was proposed for laboratory-based screening of sulfate in water and soil; for a greater degree of accuracy and precision the analytical methods as described by the Standard Method for the Evaluation of Water and Wastewater (SMEWW) 4500 for sulfate and 4110 B for anions (Rice et al., 2012) were recommended. The SMEWW method 4500 for sulfate includes additional reagents to stabilize the barium sulfate precipitate, a user-generated calibration curve, and additional QA/QC; SMEWW method 4110 B can detect lower anion concentrations but is not appropriate for seawater samples. Based on ruggedness and other factor analysis studies as well as laboratory visits (Chapters 6, 8, and 9), these major sources of variability in the FM were identified using the sulfate photometer test kit:

- Soil mass,
- Suspended solids or color in the filtered sample extract,
- Incorrect or out-of-date reagents, and
- Sulfate calibration curve.

For sulfate determination an accurate soil mass can be obtained if the soil is dried to a constant mass and its mass weighed on an analytical balance; these two requirements limit the portability of the method. In laboratory studies, suspended particles or color present in sample extracts interfered with sulfate measurements and caused either an invalid reading when the sample blank had a higher photometer response than the reacted soil extract or an elevated sulfate concentration when the suspended particles or color were not effectively subtracted from the sample with the sample blank (Chapters 5, 9). Attempts to clarify the soil extract included acid addition, a 1:1 water-to-soil ratio in the soil extraction, serial gravity filtration using Whatman 4 and Whatman 42 filters, centrifugation, and vacuum filtration through a membrane filter. One effective combination for clearing the sample extract was acid addition followed by at least one hr of settling time, gravity filtration through a Whatman 41 filter, and finally vacuum filtration through a 0.45-micron filter. Vacuum filtration through a 0.45-micron membrane filter was recommended as a final filtration step. Also recommended were separate 3:1 water-to-soil extracts for chloride and sulfate, so that acid could be added directly to the unfiltered extract, if needed. If acid were not needed, only one extract has to be filtered for chloride and sulfate determinations. A photometer with factory-programmed sulfate calibration curves gave reasonable results provided the curve was routinely checked, as the potency of the reagents used in the method varied by lot number and possibly with the age of the reagents. A sulfate check standard and associated reagent blank were included in the proposed revised FM to help to guard against bad reagents, contamination of dilution water, or a mismatched photometer response.

13.6 Proposed Revisions to the FM

Proposed revisions to the FMs for pH, resistivity, chloride and sulfate were sent to project team members, 18 commercial laboratories, and the District and State Material Offices. The revised methods were demonstrated at FDOT’s Districts 1 and 7 Materials Office and State Material Office. Comments were received from those laboratory managers and operators. Changes that stemmed from these comments included

- For the FM for minimum resistivity, a shift in the placement of routine checks of dilution water and a calibration standard from test procedure to a new best practice section;

- For the FMs for chloride and sulfate, addition of the ion chromatography method Section 4110 B from Standard Methods for the Examination of Water and Wastewater (Rice, 2012) as an acceptable method for sulfate and chloride analyses; procedural steps that clearly include both water and soil extract analyses; and addition of steps for high-range chloride tests, e.g., for seawater samples.

For the FMs for pH and minimum resistivity, changes that were made based on the results of ruggedness and treatment study testing of Alico Road, Angelo’s, Clermont, and Sebring soils (mines 5 through 8) were:

- Return to storing samples for pH measurements under refrigeration;

- Return to testing samples “as received” for pH and resistivity; and

- Removal of the steps for adding 0.1 g potassium chloride to pH samples.

These changes were included in the version of the FMs that were delivered to FDOT laboratories for the inter-laboratory study, with the exception for the FM for pH, where steps were added to address electrode memory effects ahead of the second inter-laboratory study (pH only). Proposed revised FMs are included in Appendix F.

14 Summary and Recommendations

The ultimate goals of this research were to improve quality, speed completion, and reduce risk in mechanically-stabilized earth (MSE) wall projects. Research objectives were (1) to assure that variability in the corrosion properties of soil (pH, minimum resistivity, chloride, and sulfate levels) due to sampling and analytical technique was much lower than variability in these levels within and between soil sources and types and thus did not inflate the risk of emplacing a corrosive soil as MSE wall backfill, (2) that the number of soil type samples analyzed prior to acceptance of a backfill was appropriate, based on the expected distribution of corrosion properties within the backfill, and (3) that the corrosion properties of backfill material did not change appreciably over time, especially after emplacement and over the design lifetime of the MSE wall. Corrosion properties of soil were tested with Florida Methods (FMs) 5-550, 5-551, 5-552, and 5-553 for pH, minimum resistivity, water-soluble chloride, and water-soluble sulfate, respectively.

The scope of this research included tasks to (1) review relevant literature, (2) examine trends in corrosion properties of MSE wall backfill from Districts 1 and 7 mines based on existing data, (3) determine the single-laboratory contributions to method reproducibility of factors that relate to field sampling and laboratory analysis and improve method reproducibility through changes in the methods, (4) discover the distribution of corrosion properties within and between mines for a representative sample of mines as suggested by objective (2), (5) model analytically the potential for the corrosion properties of MSE backfill to change over time with an initial focus on changes due to the ionic composition of rainfall, (6) determine multi-laboratory contributions to method reproducibility, and (7) disseminate the project results as a final report. This research was limited to 10 soils that were candidate materials for select backfill and thus low in clay, organic matter, and salt content; these soils were typical of MSE wall backfill but not likely representative of the broader variability of Florida waters and soils.

The links between the borrow pit or stockpile source, certification data, and corrosion AQC acceptance data as downloaded from LIMS were for the most part broken. A recommendation was that future documentation include the geo-coordinates (latitude and longitude, for example) of the borrow pit or stockpile of certified MSE wall backfill, and that these geo-coordinates accompany the certification data as well as the acceptance data into LIMS.

Single-operator operator studies conducted in the University of South Florida (USF) soils laboratory yielded reasonable accuracy (%RE) and precision (%RSD) for pH and minimum resistivity, but not for chloride and sulfate. Chloride and sulfate analyses were subject to interferences from suspended particles and color in soil extracts, which were significantly reduced by final filtration of the soil extract through a 0.45-micron mixed cellulose ester membrane. In multi-laboratory studies such as split-sample analyses, soil testing during laboratory visits, and an inter-laboratory study, differences seen in results indicated systematic variability between laboratories. These differences were explored through ruggedness, treatment, and other factor analysis studies, with a goal to reduce these differences in part through changes in sample processing and analysis procedures. As an example, a proposed revision to the FM for pH calls for checking the electrode condition using the slope and offset of the calibration curve before making a pH measurement. As another example, a proposed revision to the FM for minimum resistivity preferentially uses the water portion of the soil slurry for the resistivity measurement.

Divergence in corrosion test results between laboratories was seen for pH, minimum resistivity, chloride, and sulfate for one or more of the eight sands collected from mines as part of this study. Changes to the FMs for minimum resistivity, chloride, and sulfate that were trialed by USF showed promise for improving between-laboratory agreement. Split sample analyses revealed that four of the eight sands failed to meet an acceptance limit for one or more of the corrosion properties in one or more of the partnered laboratories. If the split sample analyses between two laboratories represented quality control and verification tests, at least three out of the eight sands would have required resolution testing. Reduction in a relatively high rate of resolution testing may offset additional costs associated with method improvements.

Some sands that met the specifications for MSE wall backfill had high minimum resistivity (low conductivity) and thus low ionic strength, and were a challenge for pH measurements. Potassium chloride, a neutral salt, is a possible amendment to soil samples for pH testing. Three advantages to the addition of 0.1 g of potassium chloride to 100 g of soil sample were: the pH reading was faster, more stable, and was more likely to represent the *in-situ* soil pH; the major disadvantage, however, was a drop of ~0.5 pH units in 1:1 soil:water solutions. Such a shift would likely disqualify some of Florida’s sands as candidates for MSE wall backfill. The use of potassium chloride or calcium chloride to adjust the ionic strength of soil solutions during pH measurement was not recommended at this time. The observed downward shift in pH in sandy soils with neutral salt addition, however, may indicate that these soils have significant total acidity. Recommended was further investigation of the relationship between metal corrosion rates in select backfill and soil acidity, where soil acidity is determined as both proton activity (electrochemical pH measurement) and exchangeable acidity.

Replicate studies of mined soils for each corrosion FM produced an estimate of test error that included contributions from material properties, environmental influences, and sampling, processing, and single-operator testing (method repeatability) of soils. For each FM, its test error estimate was adjusted to include the multi-laboratory testing (method reproducibility) contribution. The adjusted estimate was incorporated into a method operating characteristic (OC) curve, which had a Type I (α) error of 0.01 and a Type II (β) error of 0.05; the OC curve related the buyer’s statistical power ($1-\beta$) to accept a good backfill to the number of samples, test error, and acceptance limit(s).

Changes to the quality assurance (QA) plan for acceptance quality characteristics (AQC) of backfill corrosion properties were recommended based on research outcomes. These changes had as their focus an improvement in the buyer’s statistical power to accept good backfill material through reductions in test error associated with material properties, sample processing, and laboratory procedures. Recommended changes included (1) proposed revisions to the FMs for pH, minimum resistivity, chloride, and sulfate, respectively; (2) an increase in the number of independent samples tested for pH and minimum resistivity; (3) a revised acceptance limit for minimum resistivity; (4) method operator training and independent audits; (5) an inter-laboratory study post-implementation of the revised methods; and (6) re-evaluation of the need for chloride and sulfate testing for backfill above a pre-determined minimum resistivity. Recommended changes were outlined below:

- *Revise the FMs for pH, minimum resistivity, chloride and sulfate.* Proposed revisions to the FMs included (1) minor edits to method grammar, organization, and units of measure; (2) updates to the apparatus and reagents sections, with a hazardous materials note as appropriate; (3) step-by-step instructions to facilitate method oversight; (4) one or more QA/QC procedures; and (5) a new section for method precision and bias.

- *Increase the number of independent samples per soil type for pH and minimum resistivity.* Recommended for pH were at least three independent pH samples per soil type tested both pre-construction and post-emplacement. Recommended for minimum resistivity were at least two independent minimum resistivity samples per soil type tested both pre-construction and post-emplacement and an increase in the acceptance limit for minimum resistivity to 4,000 ohm-cm.

- *Conduct operator training and routine on-site laboratory audits of the FMs*. Operator training was recommended for all FMs, for example, training through a video demonstration of each method as well as method outcomes for both well-executed and poorly-executed procedures. Also recommended for FMs were routine independent audits, which provide oversight on method performance and put the method and operator in a context that includes environmental influences (temperature, noise, dust, crowding), laboratory practices, and pressure for time.

- *Perform a Florida-wide inter-laboratory study of the revised FMs*. A Florida-wide inter-laboratory study of the revised FMs within a year of adoption was recommended to assure that FDOT and commercial laboratories were proficient with the revised methods and to establish for each FM the method reproducibility.

- *Re-evaluate the FMs for chloride and sulfate.* A review of Florida-wide post-revision chloride and sulfate results for MSE wall backfill after a two-year data collection period was recommended to assess if further testing of chloride and sulfate were necessary for select backfill above a pre-determined minimum resistivity.

Geochemical modeling with the U. S. Geological Survey (USGS) model PHREEQC for a conservative case of a low ionic strength and poorly buffered sandy (quartz) backfill revealed that in a few years’ time the pore water of stockpiled or emplaced backfill could equilibrate with infiltrating rainfall. The model results suggested that a soil’s buffering capacity might be an important consideration when metal is used as reinforcement in MSE wall backfill. Field and laboratory testing of candidate sands to calibrate the model were recommended ahead of any proposed changes to the QA plan based on model results.

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Appendix A Ruggedness Study Results

Statistically-significant results are highlighted.

A.1 Mine 1 Wimauma Sand

Table A-1 Wimauma Sand Ruggedness Study Results for pH

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	1	2	1	2	2	1	2	1
F	f	30	0	0	30	30	0	0	30
G	g	V	G	G	V	G	V	V	G
pH Results		4.55	4.92	4.49	4.69	4.68	4.41	4.90	4.52

A	Transport in cooler (~15°C) (CT)
a	Transport under ambient conditions (~30°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~23°C) (WS)
C	Test "as is" (wet)
c	Air-dried, sieved (dry)
D	100 mL of sample (ML)
d	100 g of sample (G)
E	pH electrode 1 (ATC, refillable) (1)
e	pH electrode 2 (No ATC, not refillable) (2)
F	30 min equilibration, stirred 3 x (30)
f	Stirred once, no equilibration (0)
G	Stir vigorously (V)
g	Stir gently so as not to entrain air (G)
Note 1	Sampling date was 5/8/2014 and ruggedness study date was 5/20/2014
Note 2	Electrode 1: 13-62-AP55 (Accumet), 98.1% and 4.7 mV; 98.6% and 6.5 mV
Note 3	Electrode 2: WD-35801-00 (Oakton), 100.3%, 13.0 mV

Table A-2 Wimauma Sand Significance of Ruggedness Study for pH

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.66	0.19				Higher if transported cool; not significant
a	4.63	0.21	0.04	0.863	0.815	
B	4.64	0.22				Higher if stored warm; not significant
b	4.65	0.19	-0.01	0.824	0.947	
C	4.66	0.18				Higher if tested “as is”; not significant
c	4.64	0.22	0.02	0.748	0.894	
D	4.72	0.22				Higher for a 100-mL sample; not significant
d	4.57	0.14	0.16	0.488	0.275	
E	4.49	0.06				Higher for electrode 2; significant
e	4.80	0.13	-0.31	0.237	0.005	
F	4.61	0.09				Higher if not equilibrated; not significant
f	4.68	0.27	-0.07	0.099	0.637	
G	4.64	0.21				Higher if stirred gently; not significant
g	4.65	0.20	-0.02	0.924	0.920	

Table A-3 Wimauma Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	100	100	50	50	50	50	100	100
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1	0.5	0.5	1	1	0.5	0.5	1
G	g	no	yes	yes	no	yes	no	no	yes
Resistivity Results (ohm-cm)		47,500	54,000	43,000	63,000	41,000	56,500	59,000	55,000

A	Transport in cooler (~15°C) (CT)
a	Transport under ambient conditions (~30°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~23°C) (WS)
C	Test "as is" (wet)
c	Air-dried, sieved (dry)
D	DI water increments of 100 mL (100)
d	DI water increments of 50 mL (50)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	0.5 kg soil (0.5)
G	Electrode not covered (no)
g	Electrode covered (yes)
Note 1	Sampling date was 5/8/2014 and ruggedness study date was 5/20/2014
Note 2	DI water resistivity: 690,000 small soil box; 565,000 large soil box
Note 3	4000 ohm-cm conductivity standard: 4,250 ohm-cm at 24.0°C

Table A-4 Wimauma Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	51,900	8,680				Higher for transport under ambient conditions; not significant
a	52,900	8,090	-1,000	0.910	0.872	
B	49,800	6,960				Higher for storage at room temperature; not significant
b	55,000	8,640	-5,250	0.731	0.380	
C	47,600	8,060				Higher for testing a dried sample; not significant
c	57,100	4,050	-9,500	0.288	0.080	
D	53,900	4,770				Higher for water increments of 100 mL; not significant
d	50,900	10,600	3,000	0.221	0.625	
E	50,500	6,360				Higher for large soil box; not significant
e	54,300	9,570	-3,750	0.520	0.538	
F	51,600	9,500				Higher for 0.5 kg soil; not significant
f	53,100	7,050	-1,500	0.637	0.808	
G	56,500	6,570				Higher if electrode is not covered; not significant
g	48,300	7,270	8,250	0.871	0.143	

Table A-5 Wimauma Sand Ruggedness Study Results for Sulfate

Factors		Sulfate Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	110	60	110	60	110	60	110	60
D	d	1	1	2	2	2	2	1	1
E	e	1	2	1	2	2	1	2	1
F	f	RB	US	US	RB	RB	US	US	RB
G	g	no	yes	yes	no	yes	no	no	yes
Sulfate Results (ppm)		21	15	39	15	48	24	9	21

A	Transport in cooler (~15°C) (CT)
a	Transport under ambient conditions (~30°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~23°C) (WS)
C	Oven dry at 110°C, sieve (110)
c	Oven dry at 60°C, sieve (60)
D	Range 1 factory default (1)
d	Range 2 factory default (2)
E	Extraction method 1: 3 to 1 extraction; membrane filtration (1)
e	Extraction method 2: 1 to 1 extraction; 3:1 dilution; membrane filtration (2)
F	Reagent blank (RB)
f	Unreacted sample blank (US)
G	No sample spike (no)
g	Spiked sample to 20 ppm (yes)
Note 1	Sampling date was 5/8/2014 and ruggedness study date was 5/21/2014
Note 2	20 ppm check standard: 19 ppm

Table A-6 Wimauma Sand Significance of Ruggedness Study for Sulfate

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Sulfate Was:
A	23	11				Higher if transported under ambient conditions; not significant
a	26	16	-3	0.565	0.773	
B	27	14				Higher if stored cold; not significant
b	21	13	6	0.859	0.560	
C	29	18				Lower if dried at 60°C; significantly lower standard deviation
c	19	5	10	0.051	0.291	
D	17	6				Higher if tested on Range 2; not significant
d	32	15	-15	0.154	0.108	
E	26	9				Higher if extracted with 3:1 dilution; not significant
e	22	18	4	0.267	0.664	
F	26	15				Higher if tested with a reagent blank; not significant
f	22	13	4	0.843	0.664	
G	17	7				Higher if sample spiked with 20 ppm sulfate; not significant
g	31	15	-14	0.202	0.158	

A.2 Mine 2 Jahna Sand

Table A-7 Jahna Sand Ruggedness Study Results for pH

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	yes	no	yes	no	no	yes	no	yes
F	f	no	yes	yes	no	no	yes	yes	no
G	g	V	G	G	V	G	V	V	G
pH Results		4.79	4.66	4.71	4.70	4.98	4.60	4.59	4.69
A	Transport in cooler (~18°C) (CT)								
a	Transport under ambient conditions (~30°C) (WT)								
B	Store in refrigerator (~4°C) (CS)								
b	Store at room temperature (~23°C) (WS)								
C	Test "as is" (wet)								
c	Air-dried, sieved (dry)								
D	100 mL (ML)								
d	100 g (G)								
E	pH measurement with temperature sensed (23°C, 98.9% slope, 5.3 mV) (yes)								
e	pH measurement without temperature sensed (25°C, 99.3% slope, 5.9 mV) (no)								
F	No salt amendment (no)								
f	Amended with 0.1 g KCl (yes)								
G	Stir vigorously (V)								
g	Stir gently so as not to entrain air (G)								
Note 1	Sampling date was 5/29/2014 and ruggedness study date was 6/7/2014								
Note 2	Electrode/meter AP85/13-620-AP55								

Table A-8 Jahna Sand Significance of Ruggedness Study for pH

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.72	0.05				The same if transported cool or warm; not significant
a	4.72	0.18	0.00	0.078	1.000	
B	4.76	0.17				Higher if stored cold; not significant
b	4.67	0.06	0.09	0.102	0.374	
C	4.77	0.16				Higher if tested "as is"; not significant
c	4.66	0.05	0.11	0.062	0.263	
D	4.68	0.08				Higher for a 100 g sample; not significant
d	4.75	0.16	-0.07	0.298	0.503	
E	4.70	0.08				Higher if temperature is not sensed; not significant
e	4.73	0.17	-0.04	0.230	0.723	
F	4.79	0.13				Lower if amended with 0.1 g KCl; not significant
f	4.64	0.06	0.15	0.184	0.085	
G	4.67	0.09				Higher if stirred gently so as not to entrain air; not significant
g	4.76	0.15	-0.09	0.477	0.345	

Table A-9 Jahna Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	100	100	50	50	50	50	100	100
E	e	no	yes	no	yes	yes	no	yes	no
F	f	1.0	0.5	0.5	1.0	1.0	0.5	0.5	1.0
G	g	yes	no	no	yes	no	yes	yes	no
Resistivity Results (ohm-cm)		125,000	185,000	150,000	140,000	160,000	130,000	150,000	135,000

A	Transport in cooler (~18°C) (CT)
a	Transport under ambient conditions (~30°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~23°C) (WS)
C	Test "as is" (wet)
c	Air-dried, sieved (dry)
D	DI water increments of 100 mL (100)
d	DI water increments of 50 mL (50)
E	C1 & P1 and C2 & P2 terminals not shorted (no)
e	C1 & P1 and C2 & P2 terminals shorted (yes)
F	1.0 kg soil (1.0)
f	0.5 kg soil (0.5)
G	Soil above electrode (yes)
g	Soil not above electrode (no)
Note 1	Sampling date was 5/29/2014 and ruggedness study date was 6/7/2014
Note 2	Soil slurry temperatures were ~22°C (21.7 to 22.4)
Note 3	No calibration data recorded.

Table A-10 Jahna Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	150,000	25,500				Higher for cool transport; not significant
a	144,000	13,800	6,250	0.339	0.681	
B	150,000	28,000				Higher for cold storage; not significant
b	144,000	7,500	6,250	0.058	0.681	
C	146,000	14,900				Higher for dried soil; not significant
c	148,000	25,300	-1,250	0.408	0.935	
D	149,000	26,300				Higher for water increments of 100 mL; not significant
d	145,000	12,900	3,750	0.274	0.806	
E	135,000	10,800				Higher with terminals shorted; not significant
e	159,000	19,300	-23,800	0.365	0.075	
F	140,000	14,700				Higher with 0.5 kg soil; not significant
f	154,000	22,900	-13,800	0.488	0.351	
G	136,000	11,100				Higher with soil below electrode; not significant
g	158,000	21,000	-21,300	0.321	0.124	

A.3 Mine 3 Youngquist Sand

Table A-11 Youngquist Sand Ruggedness Study Results for pH

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	1	2	1	2	2	1	2	1
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		8.12	8.16	8.16	8.19	8.20	8.03	8.07	8.02
A	Transport in cooler (~18°C) (CT)								
a	Transport under ambient conditions (~30°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~23°C) (WS)								
C	Test "as is" (wet)								
c	Air-dried, sieved (dry)								
D	100 mL + 100 mL water (ML)								
d	30 g + 30 g water (G)								
E	Electrode/meter 1 (1)								
e	Electrode/meter 2 (2)								
F	30 min equilibration with stirring every 10 min (30)								
f	60 min equilibration with stirring every 10 min (60)								
G	No stir right before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 6/19/2014 and ruggedness study date was 7/2/2014								
Note 2	Meter/electrode 1: AP85/13-62-AP55; slope = 99.1%, offset = 3.0 mV								
Note 3	Meter/electrode 2: AB150/13-620-631; slope = 98.9%, offset = 5.8 mV								

Table A-12 Youngquist Sand Significance of Ruggedness Study for pH

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	8.16	0.03				Higher for cooler transport; not significant
a	8.08	0.08	0.08	0.115	0.128	
B	8.13	0.07				Higher for cold storage; not significant
b	8.11	0.08	0.02	0.899	0.755	
C	8.14	0.06				Higher for “as is”; not significant
c	8.10	0.09	0.04	0.475	0.497	
D	8.09	0.06				Higher for a 30-g sample; not significant
d	8.15	0.08	-0.05	0.684	0.331	
E	8.08	0.07				Higher for electrode 2; not significant
e	8.16	0.06	-0.07	0.815	0.160	
F	8.13	0.08				Higher for 30 min equilibration; not significant
f	8.11	0.07	0.03	0.708	0.622	
G	8.10	0.07				Higher for stir immediately before testing; not significant
g	8.14	0.08	-0.03	0.830	0.558	

Table A-13 Youngquist Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	SS	SS	WS	WS	WS	WS	SS	SS
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1.0	1.5	1.5	1.0	1.0	1.5	1.5	1.0
G	g	yes	no	no	yes	no	yes	yes	no
Resistivity Results (ohm-cm)		9,250	8,500	4,300	6,150	4,950	3,700	7,400	7,950

A	Transport in cooler (~18°C)
a	Transport under ambient conditions (~30°C)
B	Store in refrigerator (~ 4°C)
b	Store at room temperature (~23°C)
C	Test "as is"
c	Air-dried, sieved, 10% water added and allowed to equilibrate overnight
D	Mostly soil (when sample is saturated) (SS)
d	Mostly water (when sample is saturated) (WS)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	1.5 kg soil (1.5)
G	Rinse box with DI water between measurements (yes)
g	Do not rinse box with DI water between measurements (no)
Note 1	Sampling date was 6/19/2014 and ruggedness study date was 7/2/2014
Note 2	Resistivity of DI (dilution) water was 810,000 ohm-cm
Note 3	Resistivity of a 4,000 ohm-cm conductivity standard was 4,000 ohm-cm

Table A-14 Youngquist Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	7,050	2,260				Resistivity was higher for cool transport; not significant
a	6,000	2,010	1,050	0.854	0.514	
B	6,600	2,690				Resistivity was higher for cold storage; not significant
b	6,450	1,620	150	0.425	0.927	
C	6,480	2,280				Resistivity was higher for dried soil; not significant
c	6,580	2,160	-100	0.933	0.951	
D	8,280	790				Resistivity was higher for soil slurry; significant
d	4,780	1,050	3,500	0.653	0.002	
E	6,300	2,720				Resistivity was higher for large soil box; not significant
e	6,750	1,540	-450	0.374	0.783	
F	7,080	1,900				Resistivity was higher for 1.0 kg of soil; not significant
f	5,980	2,340	1,100	0.744	0.493	
G	6,630	2,330				Resistivity was higher if box rinsed between tests; not significant
g	6,430	2,110	200	0.873	0.903	

Table A-15 Youngquist Sand Ruggedness Study Results for Sulfate

Factors		Sulfate Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CC	CC	CC	CC	WW	WW	WW	WW
B	b	1	1	2	2	1	1	2	2
C	c	110	60	110	60	110	60	110	60
D	d	1	1	2	2	2	2	1	1
E	e	1	2	1	2	2	1	2	1
F	f	10	18	18	10	10	18	18	10
G	g	no	yes	yes	no	yes	no	no	yes
Sulfate Results (ppm)		45	54	36	36	66	33	60	30

A	Transport in cooler (~15°C), cold storage (~4°C) (CC)
a	Warm transport (~30°C), room temperature storage (WW)
B	100 mg soil/300 mL water (3:1 dilution) (1)
b	100 mg soil/100 mL water (1:1 dilution); diluted 3:1 post-filtration (2)
C	Oven dry at 110°C, sieve (110)
c	Oven dry at 60°C, sieve (60)
D	Filtration through Q8, acid added, then 0.45 micron membrane (1)
d	Centrifuge, acid added, then 0.45 micron membrane (2)
E	Range 1 Factory Default (1)
e	Range 2 Factory Default (2)
F	Sieved through No. 10 (2 mm) (10)
f	Sieved through No. 18 (1 mm) (18)
G	No sample spike (no)
g	Spiked sample to 20 ppm (yes)
Note 1	Sampling date was 6/19/2014 and ruggedness study date was 7/11/2014
Note 2	A 20-ppm check standard was 18 ppm on Range 1 and 22 ppm on Range 2
Note 3	A 20-ppm check standard was 16 ppm on Range 1 and 20 ppm on Range 2

Table A-16 Youngquist Sand Significance of Ruggedness Study for Sulfate

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Sulfate Was:
A	43	9				Sulfate was higher for warm transport and storage; not significant
a	47	18	-4	0.245	0.673	
B	50	14				Sulfate was higher for extraction with 3:1 dilution; not significant
b	41	13	9	0.938	0.387	
C	52	14				Sulfate was higher for soil dried at 110 C; not significant
c	38	11	14	0.702	0.173	
D	47	13				Sulfate was higher for filtration; not significant
d	43	16	4	0.779	0.673	
E	36	6				Sulfate was higher on Range 2: significant
e	54	13	-18	0.285	0.048	
F	44	16				Sulfate was higher if sieved through No. 18 sieve; not significant
f	46	13	-2	0.785	0.889	
G	44	12				Sulfate was higher if spiked with 20 ppm standard; not significant
g	47	17	-3	0.624	0.780	

A.4 Mine 4 Calhoun Sand

Table A-17 Calhoun Sand Ruggedness Study Results for pH

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	no	yes	no	yes	yes	no	yes	no
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		4.79	4.19	4.82	4.23	4.26	4.66	4.20	4.65
A	Transport in cooler (~21°C) (CT)								
a	Transport under ambient conditions (~31°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as is" (wet)								
c	Air-dried, sieved (dry)								
D	100 mL sample size (ML)								
d	100 g sample size (G)								
E	No salt amendment (no)								
e	Amendment with 0.1 g KCl (yes)								
F	30 min equilibration with stirring every 10 min (30)								
f	1 hr equilibration with stirring every 10 min (60)								
G	No stir right before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 7/14/2014 and ruggedness study date was 7/23/2014								
Note 2	Electrode/meter AB150/13-620-631; slope = 100.7% and offset = 4 mV								

Table A-18 Calhoun Sand Significance of Ruggedness Study Factors for pH

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.51	0.34				Higher if transported cool; not significant
a	4.44	0.25	0.07	0.598	0.769	
B	4.48	0.30				The same if stored cold or at room temperature; not significant
b	4.48	0.31	0.00	0.943	1.000	
C	4.52	0.33				Higher if tested “as is”; not significant
c	4.43	0.26	0.09	0.683	0.700	
D	4.46	0.31				Higher for a 100 g sample; not significant
d	4.49	0.29	-0.04	0.936	0.875	
E	4.73	0.09				Lower if amended with 0.1 g KCl; significant
e	4.22	0.03	0.51	0.128	0.000	
F	4.48	0.28				Higher if equilibrated for 30 min; not significant
f	4.47	0.32	0.02	0.828	0.946	
G	4.47	0.30				Higher if stirred immediately before testing; not significant
g	4.48	0.30	-0.01	0.981	0.964	

Table A-19 Calhoun Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	SS	SS	WS	WS	WS	WS	SS	SS
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1.0	1.5	1.5	1.0	1.0	1.5	1.5	1.0
G	g	yes	no	no	yes	no	yes	yes	no
Resistivity Results (ohm-cm)		110,000	96,500	39,000	40,000	48,000	33,000	108,000	104,000

A	Transport in cooler (~21°C) (CT)
a	Transport under ambient conditions (~31°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as is" (wet)
c	Air-dried, sieved, 10% water added and allowed to equilibrate overnight (dry)
D	Mostly soil (when sample is saturated) (SS)
d	Mostly water (when sample is saturated) (WS)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	1.5 kg soil (1.5)
G	Rinse box with DI water between measurements (yes)
g	Do not rinse box with DI water between measurements (no)
Note 1	Sampling date was 7/14/2014; ruggedness study date was 7/23/2014
Note 2	DI water resistivity was 780,000 ohm-cm at ~24 C
Note 3	4,000 ohm-cm conductivity standard was 4,000 ohm-cm at ~24°C

Table A-20 Calhoun Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Average	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	71,400	37,200				Higher if transported under ambient conditions; not significant
a	73,300	38,300	-1,880	0.962	0.946	
B	71,900	37,200				Higher if stored at room temperature; not significant
b	72,800	38,400	-875	0.957	0.975	
C	76,300	38,000				Higher if tested "as is"; not significant
c	68,400	37,000	7,880	0.967	0.777	
D	104,600	5,960				Higher if tested as a slurry of mostly soil; significant
d	40,000	6,160	64,600	0.958	0.000	
E	71,500	41,100				Higher if tested in the large soil box; not significant
e	73,100	34,100	-1,630	0.766	0.953	
F	75,500	36,600				Higher if tested with 1 kg of soil; not significant
f	69,100	38,610	6,380	0.932	0.819	
G	72,800	42,000				Higher if soil box rinsed between tests; not significant
g	71,900	33,100	875	0.707	0.975	

A.5 Mine 5 Angelo’s Sand

Table A-21 Angelo’s Sand Ruggedness Study Results for pH (Replicate 1)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	1	2	1	2	2	1	2	1
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		4.63	4.53	5.26	4.55	4.53	4.57	4.54	4.53
A	Transport in cooler (~19°C) (CT)								
a	Transport under ambient conditions (~24°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as received" (wet)								
c	Dried at 60°C, No. 10 sieve (dry)								
D	100 mL (ML)								
d	100 g (G)								
E	Electrode 1, 13-620-631 (99.2% slope, 3.3 mV, 25.0°C) (1)								
e	Electrode 2, 13-620-631 (100% slope, -0.8 mV, 25.4°C) (2)								
F	30-min equilibrium period with stirring every 10 min (30)								
f	60-min equilibrium period with stirring every 10 min (60)								
G	No stir before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 9/17/2014 and ruggedness study dates were 9/27/2014								
Note 2	pH meter AB150								

Table A-22 Angelo’s Sand Significance of Ruggedness Study for pH (Replicate 1)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.74	0.35				Higher if transported cool; not significant
a	4.54	0.02	0.20	0.001	0.294	
B	4.57	0.05				Higher if stored warm; not significant
b	4.72	0.36	-0.16	0.007	0.426	
C	4.74	0.35				Higher if tested “as received”; not significant
c	4.55	0.02	0.19	0.001	0.308	
D	4.56	0.05				Higher for a 100 g sample; not significant
d	4.73	0.36	-0.17	0.008	0.380	
E	4.75	0.34				Higher for electrode 1; not significant
e	4.54	0.01	0.21	0.000	0.268	
F	4.56	0.05				Higher for a 60-min equilibrium, not significant
f	4.73	0.36	-0.17	0.008	0.395	
G	4.57	0.04				Higher if stirred immediately before testing; not significant
g	4.71	0.37	-0.14	0.004	0.475	

Table A-23 Angelo’s Sand Ruggedness Study Results for pH (Replicate 2)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	1	2	1	2	2	1	2	1
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		4.61	4.55	4.64	5.05	4.53	4.58	4.54	4.58
A	Transport in cooler (~19°C) (CT)								
a	Transport under ambient conditions (~24°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as received" (wet)								
c	Dried at 60°C, No. 10 sieve (dry)								
D	100 mL (ML)								
d	100 g (G)								
E	Electrode 1, 13-620-631 (99.5% slope, 28 mV, 24.8 C) (1)								
e	Electrode 2, 13-620-631 (100.5% slope, -1.0 mV, 25.0 C) (2)								
F	30-min equilibrium period with stirring every 10 min (30)								
f	60-min equilibrium period with stirring every 10 min (60)								
G	No stir before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 9/17/2014 and ruggedness study dates were 9/29/2014								
Note 2	pH meter AB150								

Table A-24 Angelo's Sand Significance of Ruggedness Study for pH (Replicate 2)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.71	0.23				Higher if transported cool; not significant
a	4.56	0.03	0.15	0.005	0.226	
B	4.57	0.04				Higher if stored warm; not significant
b	4.70	0.24	-0.13	0.011	0.300	
C	4.58	0.05				Higher if tested dried and sieved; not significant
c	4.69	0.24	-0.11	0.034	0.406	
D	4.57	0.03				Higher for a 100 g sample; not significant
d	4.70	0.24	-0.13	0.008	0.320	
E	4.60	0.03				Higher for electrode 2; not significant
e	4.67	0.26	-0.07	0.005	0.631	
F	4.69	0.24				Higher for a 30-min equilibrium, not significant
f	4.58	0.05	0.11	0.021	0.384	
G	4.70	0.24				Higher if not stirred immediately before testing; not significant
g	4.58	0.05	0.12	0.026	0.362	

Table A-25 Angelo's Sand Significance of Ruggedness Study Factors for pH Obtained from the Combined Results of Replicate Studies

Factor	*F* Statistic[1]	Conclusion
A, a	4.43	Cool vs warm transport is not significant
B, b	1.97	Cold vs warm storage is not significant
C, c	0.02	"As received" vs dried, sieved is not significant
D, d	2.26	100 mL vs 100 g is not significant
E, e	0.12	Electrode 1 vs 2 is not significant
F, f	0.00	30-min vs 60-min equilibrium period is not significant
G, g	0.00	Not stirring vs stirring before testing is not significant

[1] Calculated as described in ASTM C1067 (2007); an *F* statistic ≥ 5.59 is significant at the 95% confidence level.

Table A-26 Angelo’s Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	DI	DI	DI-S	DI-S	DI-S	DI-S	DI	DI
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1.0	0.5	0.5	1.0	1.0	0.5	0.5	1.0
G	g	no	yes	yes	no	yes	no	no	yes
Resistivity Results (ohm-cm)		17,000	21,000	16,500	15,000	16,500	16,000	22,000	16,000

A	Transport in cooler (~19°C) (CT)
a	Transport under ambient conditions (~24°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as received" (wet)
c	Dried at 60°C, No. 10 sieve (dry)
D	DI water (>1,000,000 ohm-cm; measured in large soil box) (DI)
d	DI water, sodium chloride added (175,000 ohm-cm, measured in large soil box) (DI-S)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	0.5 kg soil (0.5)
G	No equilibrium period (no)
g	Equilibrium period of 30 min after adding 20% dilution water (yes)
Note 1	Sampling date was 9/17/2014 and ruggedness study dates were 9/27/2014 & 9/28/2014
Note 2	4,000 ohm-cm conductivity standard was 4,000 ohm-cm at ~25.0°C measured in the large box

Table A-27 Angelo's Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	17,400	2,560				Higher for transport under ambient conditions; not significant
a	17,600	2,930	-250	0.832	0.902	
B	17,600	2,290				Higher for cold storage; not significant
b	17,400	3,150	250	0.613	0.902	
C	18,000	2,680				Higher for "as received" soil; not significant
c	17,000	2,710	1,000	0.985	0.618	
D	19,000	2,940				Higher for DI water; not significant
d	16,000	707	3,000	0.043	0.095	
E	16,400	479				Higher for large soil box; not significant
e	18,600	3,400	-2,250	0.009	0.238	
F	16,100	854				Higher for 0.5 kg soil; not significant
f	18,900	3,070	-2,750	0.064	0.135	
G	17,500	3,110				No difference with and without an equilibrium period; not significant
g	17,500	2,350	0	0.655	1.000	

Table A-28 Angelo’s Sand Ruggedness Study Results for Sulfate

Factors		Sulfate Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CC	CC	CC	CC	WW	WW	WW	WW
B	b	1	1	2	2	1	1	2	2
C	c	110	60	110	60	110	60	110	60
D	d	no	no	yes	yes	yes	yes	no	no
E	e	1	2	1	2	2	1	2	1
F	f	no	yes	yes	no	no	yes	yes	no
G	g	no	yes	yes	no	yes	no	no	yes
Sulfate Results (ppm)		21	69	15	8	63	21	30	24

A	Transport in cooler, store in refrigerator (CC)
a	Transport under ambient conditions, store at room temperature (WW)
B	Reagent Lot 4120 (1)
b	Reagent Lot 4202 (2)
C	Oven dry at 110°C, sieve (110)
c	Oven dry at 60°C, sieve (60)
D	No added acid (no)
d	Added acid (yes)
E	Range 1 factory default (1)
e	Range 2 factory default (2)
F	No membrane filtration (no)
f	Membrane filtration (yes)
G	No sample spike (no)
g	Spiked sample to 20 ppm (yes)
Note 1	Sampling date was 9/17/2014 and ruggedness study date was 9/28/2014
Note 2	20 ppm check standard: 24 ppm, range 1, lot 4120; 27 ppm, range 2, lot 4204

Table A-29 Angelo's Sand Significance of Ruggedness Study for Sulfate

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Sulfate Was:
A	28	28				Higher for transport and storage under ambient conditions; not significant
a	35	19	-7	0.572	0.724	
B	44	26				Higher for reagent lot 4120; not significant
b	19	10	25	0.139	0.132	
C	32	21				Higher if dried at 110°C; not significant
c	31	27	1	0.730	0.922	
D	36	22				Higher if no added acid; not significant
d	27	25	9	0.869	0.599	
E	20	4				Higher if tested on Range 2; not significant
e	43	29	-23	0.008	0.175	
F	29	24				Higher for membrane filtration; not significant
f	34	24	-5	0.969	0.789	
G	20	9				Higher with a 20 ppm sulfate spike; not significant
g	43	27	-23	0.104	0.164	

A.6 Mine 6 Sebring Sand

Table A-30 Sebring Sand Ruggedness Study Results for pH (Replicate 1)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	1	2	1	2	2	1	2	1
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		4.69	4.42	4.39	4.36	4.39	4.39	4.38	4.32
A	Transport in cooler (~19°C) (CT)								
a	Transport under ambient conditions (~24°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as received" (wet)								
c	Dried at 60°C, No. 10 sieve (dry)								
D	100 mL (ML)								
d	100 g (G)								
E	Electrode 1, 13-620-631 (99.6% slope, 1.5 mV, 24.7 C) (1)								
e	Electrode 2, 13-620-631 (99.2% slope, 2.8 mV, 24.5 C) (2)								
F	30-min equilibrium period with stirring every 10 min (30)								
f	60-min equilibrium period with stirring every 10 min (60)								
G	No stir before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 10/15/2014 and ruggedness study dates were 10/27/2014								
Note 2	pH meter AB150								

Table A-31 Sebring Sand Significance of Ruggedness Study for pH (Replicate 1)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.47	0.15				Higher if transported cool; not significant
a	4.37	0.03	0.10	0.034	0.268	
B	4.47	0.15				Higher if stored cold; not significant
b	4.36	0.03	0.11	0.030	0.190	
C	4.46	0.15				Higher if tested “as received”; not significant
c	4.37	0.04	0.09	0.066	0.297	
D	4.45	0.16				Higher for a 100 mL sample; not significant
d	4.38	0.02	0.07	0.003	0.427	
E	4.45	0.17				Higher for electrode 1; not significant
e	4.39	0.03	0.06	0.011	0.499	
F	4.44	0.17				Higher for a 30-min equilibrium, not significant
f	4.40	0.02	0.05	0.004	0.616	
G	4.46	0.16				Higher if not stirred immediately before testing; not significant
g	4.38	0.04	0.08	0.059	0.392	

Table A-32 Sebring Sand Ruggedness Study Results for pH (Replicate 2)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	1	2	1	2	2	1	2	1
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		4.39	4.35	4.34	4.34	4.37	4.35	4.32	4.33
A	Transport in cooler (~19°C) (CT)								
a	Transport under ambient conditions (~24°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as received" (wet)								
c	Dried at 60°C, No. 10 sieve (dry)								
D	100 mL (ML)								
d	100 g (G)								
E	Electrode 1, 13-620-631 (99.5% slope, 1.3 mV, 24.5 C) (1)								
e	Electrode 2, 13-620-631 (99.4% slope, 1.8 mV, 24.3 C) (2)								
F	30-min equilibrium period with stirring every 10 min (30)								
f	60-min equilibrium period with stirring every 10 min (60)								
G	No stir before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 10/15/2014 and ruggedness study dates were 10/27/2014								
Note 2	pH meter AB150								

Table A-33 Sebring Sand Significance of Ruggedness Study for pH (Replicate 2)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	4.36	0.02				Higher if transported cool; not significant
a	4.34	0.02	0.01	0.910	0.471	
B	4.37	0.02				Higher if stored cold; significant
b	4.33	0.01	0.03	0.285	0.023	
C	4.36	0.03				Higher if tested “as received”; not significant
c	4.34	0.01	0.01	0.084	0.471	
D	4.35	0.03				Higher for a 100 g sample; not significant
d	4.35	0.01	0.00	0.231	0.888	
E	4.35	0.03				Higher for electrode 1; not significant
e	4.35	0.02	0.01	0.710	0.670	
F	4.36	0.03				Higher for a 30-min equilibrium, not significant
f	4.34	0.01	0.02	0.303	0.301	
G	4.35	0.03				Higher if not stirred immediately before testing; not significant
g	4.35	0.02	0.00	0.395	0.888	

TableA-34 Sebring Sand Significance of Ruggedness Study Factors for pH Obtained from the Combined Results of Replicate Studies

Factor	*F* Statistic[1]	Conclusion
A, a	1.73	Cool vs warm transport is not significant
B, b	5.35	Cold vs warm storage is significant (borderline)
C, c	1.43	“As received” vs dried, sieved is not significant
D, d	0.27	100 mL vs 100 g is not significant
E, e	0.27	Electrode 1 vs Electrode 2 is not significant
F, f	0.20	30-min vs 60-min equilibrium period is not significant
G, g	0.47	Not stirring vs stirring before testing is not significant

[1] Calculated as described in ASTM C1067 (2007); an *F* statistic ≥ 5.59 is significant at the 95% confidence level.

Table A-35 Sebring Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	DI	DI	DI-S	DI-S	DI-S	DI-S	DI	DI
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1.0	0.5	0.5	1.0	1.0	0.5	0.5	1.0
G	g	no	yes	yes	no	yes	no	no	yes
Resistivity Results (ohm-cm)		36,500	42,500	37,000	30,000	34,500	28,500	47,000	26,500

A	Transport in cooler (~19°C) (CT)
a	Transport under ambient conditions (~24°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as received" (wet)
c	Dried at 60°C, No. 10 sieve (dry)
D	DI water (>1,000,000 ohm-cm; measured in large soil box) (DI)
d	DI water, sodium chloride added (175,000 ohm-cm, measured in large soil box) (DI-S)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	0.5 kg soil (0.5)
G	No equilibrium period (no)
g	Equilibrium period of 30 min after adding 20% dilution water (yes)
Note 1	Sampling date was 10/15/2014 and ruggedness study dates were 10/28/2014
Note 2	4,000 ohm-cm conductivity standard was 4,000 ohm-cm at ~24.0°C measured in the large box

Table A-36 Sebring Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	36,500	5,120				Higher for transport under cool conditions; not significant
a	34,100	9,230	2,380	0.358	0.668	
B	35,500	5,770				Higher for cold storage; not significant
b	35,100	9,040	375	0.481	0.947	
C	38,800	5,610				Higher for “as received” soil; not significant
c	31,900	7,230	6,880	0.686	0.183	
D	38,100	8,860				Higher for DI water; not significant
d	32,500	3,940	5,630	0.216	0.290	
E	32,100	5,410				Higher for large soil box; not significant
e	38,500	7,670	-6,380	0.580	0.223	
F	31,900	4,500				Higher for 0.5 kg soil; not significant
f	38,800	7,960	-6,880	0.373	0.183	
G	35,500	8,420				Higher for no equilibrium period; not significant
g	35,100	6,650	375	0.708	0.947	

Table A-37 Ruggedness Study Results for Sulfate

Factors		Sulfate Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CC	CC	CC	CC	WW	WW	WW	WW
B	b	1	1	2	2	1	1	2	2
C	c	110	60	110	60	110	60	110	60
D	d	no	no	yes	yes	yes	yes	no	no
E	e	1	2	1	2	2	1	2	1
F	f	no	yes	yes	no	no	yes	yes	no
G	g	no	yes	yes	no	yes	no	no	yes
Sulfate Results (ppm)		9	9	6	6	9	9	9	3

A	Transport in cooler, store in refrigerator (CC)
a	Transport under ambient conditions, store at room temperature (WW)
B	Reagent Lot 4120 (1)
b	Reagent Lot 4202 (2)
C	Oven dry at 110°C, sieve (110)
c	Oven dry at 60°C, sieve (60)
D	No added acid (no)
d	Added acid (yes)
E	Range 1 factory default (1)
e	Range 2 factory default (2)
F	No membrane filtration (no)
f	Membrane filtration (yes)
G	No change (no)
g	No change (yes)
Note 1	Sampling date was 10/15/2014 and ruggedness study date was10/30/2014
Note 2	30 ppm check standard: 35 ppm, range 1, lot 4120; 41 ppm, range 2, lot 4204

Table A-38 Sebring Sand Significance of Ruggedness Study for Sulfate

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	Sulfate Was:
A	8	2				Not different for transport and storage under ambient conditions; not significant
a	8	3	0	0.39	1.00	
B	8	0				Higher for reagent lot 4120; significant
b	6	2	2	0.00	0.05	
C	8	2				Higher if dried at 110 C; not significant
c	7	3	1	0.31	0.39	
D	8	3				Higher if no added acid; not significant
d	8	2	0	0.39	1.00	
E	7	3				Higher if tested on Range 2; not significant
e	8	2	-1	0.31	0.39	
F	7	3				Higher for membrane filtration; not significant
f	8	2	-1	0.31	0.39	
G	8	2				Higher for no change, not significant
g	7	3	1	0.31	0.39	

A.7 Mine 7 Clermont Sand

Table A-39 Clermont Sand Ruggedness Study Results for pH (Replicate 1)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	KCl	$CaCl_2$	KCl	$CaCl_2$	$CaCl_2$	KCl	$CaCl_2$	KCl
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		7.55	7.16	7.84	7.38	7.05	7.31	7.15	7.70
A	Transport in cooler (~13°C) (CT)								
a	Transport under ambient conditions (~27°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as received" (wet)								
c	Dried at 60°C, No. 10 sieve (dry)								
D	100 mL sample size (ML)								
d	100 g sample size (G)								
E	Amendment with 0.1 g KCl (KCl)								
e	Amendment with 0.1 g CaCl ($CaCl_2$)								
F	30 min equilibration with stirring every 10 min (30)								
f	60 min equilibration with stirring every 10 min (60)								
G	No stir right before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 10/29/2014 and ruggedness study date was 11/7/2014								
Note 2	Electrode/meter AB150/13-620-631; slope = 99.8% and offset = 2.1 mV @ 25.3°C								

Table A-40 Clermont Sand Significance of Ruggedness Study Factors for pH (Replicate 1)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	7.48	0.29				Higher if transported cool; not significant
a	7.30	0.29	0.18	0.995	0.408	
B	7.27	0.22				Higher if stored warm; not significant
b	7.52	0.31	-0.25	0.565	0.236	
C	7.40	0.37				Higher if tested “as received”; not significant
c	7.39	0.28	0.01	0.457	0.964	
D	7.39	0.28				Higher for a 100 g sample; not significant
d	7.40	0.33	-0.00	0.790	0.982	
E	7.60	0.23				Higher if amended with 0.1 g KCl; significant
e	7.19	0.14	0.41	0.444	0.021	
F	7.42	0.28				Higher if equilibrated for 30 min; not significant
f	7.37	0.33	0.06	0.809	0.806	
G	7.35	0.17				Higher if stirred immediately before testing; not significant
g	7.44	0.39	-0.09	0.193	0.686	

Table A-41 Clermont Sand Ruggedness Study Results for pH (Replicate 2)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	KCl	$CaCl_2$	KCl	$CaCl_2$	$CaCl_2$	KCl	$CaCl_2$	KCl
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		7.55	7.28	7.81	6.98	7.16	7.59	7.23	7.67

A	Transport in cooler (~13°C) (CT)
a	Transport under ambient conditions (~27°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as received" (wet)
c	Dried at 60°C, No. 10 sieve (dry)
D	100 mL sample size (ML)
d	100 g sample size (G)
E	Amendment with 0.1 g KCl (KCl)
e	Amendment with 0.1 g CaCl ($CaCl_2$)
F	30 min equilibration with stirring every 10 min (30)
f	60 min equilibration with stirring every 10 min (60)
G	No stir right before testing (no)
g	Stir immediately before testing (yes)
Note 1	Sampling date was 10/29/2014 and ruggedness study date was 11/7/2014
Note 2	Electrode/meter AB150/13-620-631; slope = 99.8% and offset = 2.1 mV @ 25.3°C

Table A-42 Clermont Sand Significance of Ruggedness Study Factors for pH (Replicate 2)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	7.41	0.36				Higher if transported warm; not significant
a	7.41	0.26	-0.007	0.595	0.974	
B	7.40	0.21				Higher if stored warm; not significant
b	7.42	0.39	-0.027	0.341	0.904	
C	7.44	0.30				Higher if tested "as received"; not significant
c	7.38	0.32	0.057	0.940	0.801	
D	7.43	0.21				Higher for a 100 mL sample; not significant
d	7.39	0.38	0.048	0.359	0.835	
E	7.66	0.12				Higher if amended with 0.1 g KCl; significant
e	7.16	0.13	0.492	0.830	0.001	
F	7.34	0.32				Higher if equilibrated for 60 min; not significant
f	7.48	0.27	-0.138	0.785	0.540	
G	7.34	0.29				Higher if stirred immediately before testing; not significant
g	7.48	0.31	-0.143	0.907	0.525	

Table A-43 Clermont Sand Significance of Ruggedness Study Factors for pH Obtained from the Combined Results of Replicate Studies

Factor	*F* Statistic[1]	Conclusion
A, a	1.21	Cool vs warm transport is not significant
B, b	8.11	Cold vs warm storage is significant
C, c	0.03	"As received" vs dried, sieved is not significant
D, d	0.00	100 mL vs 100 g is not significant
E, e	927	0.1 g KCl vs 0.1 g $CaCl_2$ is significant
F, f	0.06	30-min vs 60-min equilibrium period is not significant
G, g	4.00	Not stirring vs stirring before testing is not significant

[1] Calculated as described in ASTM C1067 (2007); an *F* statistic ≥ 5.59 is significant at the 95% confidence level.

Table A-44 Clermont Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	DI	DI	DI-S	DI-S	DI-S	DI-S	DI	DI
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1.0	1.5	1.5	1.0	1.0	1.5	1.5	1.0
G	g	no	yes	yes	no	yes	no	no	yes
Resistivity Results (ohm-cm)		22,000	25,000	18,000	25,000	26,000	18,000	25,500	22,000

A	Transport in cooler (~13°C) (CT)
a	Transport under ambient conditions (~27°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as received" (wet)
c	Dried at 60°C, No. 10 sieve (dry)
D	DI water (>1,000,000 ohm-cm; measured in small soil box) (DI)
d	DI water, sodium chloride added (165,000 ohm-cm, measured in small soil box) (DI-S)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	1.5 kg soil (1.5)
G	No equilibrium period (no)
g	Equilibrium period of 30 min after adding 20% dilution water (yes)
Note 1	Sampling date was 10/29/2014; ruggedness study date was 11/8/2014
Note 2	4,000 ohm-cm conductivity standard was 3,850 ohm-cm at ~24.3°C

Table A-45 Clermont Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Average	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	22,500	3,320				Higher if transported under ambient conditions; not significant
a	22,900	3,710	-375	0.860	0.885	
B	22,800	3,590				Higher if stored cold; not significant
b	22,600	3,450	125	0.948	0.962	
C	22,900	3,710				Higher if tested “as received”; not significant
c	22,500	3,320	375	0.860	0.885	
D	23,600	1,890				Higher if tested with DI water; not significant
d	21,800	4,350	1,880	0.204	0.459	
E	20,000	2,310				Higher if tested in the large soil box; significant
e	25,400	479	-5,400	0.028	0.004	
F	23,800	2,060				Higher if tested with 1 kg of soil; not significant
f	21,600	4,190	2,130	0.274	0.398	
G	22,600	3,450				Higher for a 30-min equilibrium period; not significant
g	22,800	3,590	-125	0.948	0.962	

A.8 Mine 8 Alico Road Sand

Table A-46 Alico Road Sand Ruggedness Study Results for pH (Replicate 1)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	KCl	$CaCl_2$	KCl	$CaCl_2$	$CaCl_2$	KCl	$CaCl_2$	KCl
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		8.99	8.06	8.87	8.28	8.32	8.94	8.02	8.66
A	Transport in cooler (~13°C) (CT)								
a	Transport under ambient conditions (~27°C) (WT)								
B	Store in refrigerator (~ 4°C) (CS)								
b	Store at room temperature (~24°C) (WS)								
C	Test "as received" (wet)								
c	Dried at 60°C, No. 10 sieve (dry)								
D	100 mL sample size (ML)								
d	100 g sample size (G)								
E	Amendment with 0.1 g KCl (KCl)								
e	Amendment with 0.1 g CaCl ($CaCl_2$)								
F	30 min equilibration with stirring every 10 min (30)								
f	60 min equilibration with stirring every 10 min (60)								
G	No stir right before testing (no)								
g	Stir immediately before testing (yes)								
Note 1	Sampling date was 11/12/2014 and ruggedness study date was 11/23/2014								
Note 2	Electrode/meter AB150/13-620-631; slope = 98.6% and offset = 1.4 mV @ 23.9°C								

Table A-47 Alico Road Sand Significance of Ruggedness Study Factors for pH (Replicate 1)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	8.55	0.45				Higher if transported cool; not significant
a	8.49	0.40	0.07	0.851	0.836	
B	8.58	0.46				Higher if stored cold; not significant
b	8.46	0.38	0.12	0.761	0.702	
C	8.55	0.46				Higher if tested "as received"; not significant
c	8.49	0.39	0.07	0.803	0.836	
D	8.43	0.47				Higher for a 100 g sample; not significant
d	8.60	0.35	-0.17	0.636	0.585	
E	8.87	0.15				Higher if amended with 0.1 g KCl; significant
e	8.17	0.15	0.70	0.943	0.001	
F	8.56	0.33				Higher if equilibrated for 30 min; not significant
f	8.47	0.50	0.09	0.518	0.775	
G	8.56	0.48				Higher if not stirred immediately before testing; not significant
g	8.48	0.36	0.08	0.638	0.799	

Table A-48 Alico Road Sand Ruggedness Study Results for pH (Replicate 2)

Factors		pH Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	ML	ML	G	G	G	G	ML	ML
E	e	KCl	$CaCl_2$	KCl	$CaCl_2$	$CaCl_2$	KCl	$CaCl_2$	KCl
F	f	30	60	60	30	30	60	60	30
G	g	no	yes	yes	no	yes	no	no	yes
pH Results		8.85	8.11	8.95	8.13	8.28	8.84	8.17	8.67

A	Transport in cooler (~13°C) (CT)
a	Transport under ambient conditions (~27°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as received" (wet)
c	Dried at 60°C, No. 10 sieve (dry)
D	100 mL sample size (ML)
d	100 g sample size (G)
E	Amendment with 0.1 g KCl (KCl)
e	Amendment with 0.1 g CaCl ($CaCl_2$)
F	30 min equilibration with stirring every 10 min (30)
f	60 min equilibration with stirring every 10 min (60)
G	No stir right before testing (no)
g	Stir immediately before testing (yes)
Note 1	Sampling date was 11/12/2014 and ruggedness study date was 11/23/2014
Note 2	Electrode/meter AB150/13-620-631; slope = 99.1% and offset = 2.9 mV @ 23.8°C

Table A-49 Alico Road Sand Significance of Ruggedness Study Factors for pH (Replicate 2)

Factors	Avg	St Dev	Diff	*F*-tests	*t*-tests	pH Was:
A	8.51	0.45				Higher if transported cool; not significant
a	8.49	0.32	0.02	0.574	0.945	
B	8.52	0.38				Higher if stored cold; not significant
b	8.48	0.40	0.04	0.946	0.889	
C	8.56	0.39				Higher if tested "as received"; not significant
c	8.44	0.37	0.13	0.930	0.661	
D	8.45	0.37				Higher for a 100 g sample; not significant
d	8.55	0.41	-0.10	0.871	0.727	
E	8.83	0.12				Higher if amended with 0.1 g KCl; significant
e	8.17	0.08	0.66	0.503	0.000	
F	8.48	0.33				Higher if equilibrated for 60 min; not significant
f	8.52	0.44	-0.04	0.666	0.903	
G	8.50	0.40				Higher if stirred immediately before testing; not significant
g	8.50	0.38	-0.01	0.928	0.986	

Table A-50 Alico Road Sand Significance of Ruggedness Study Factors for pH Obtained from the Combined Results of Replicate Studies

Factor	*F* Statistic[1]	Conclusion
A,a	0.96	Cool vs warm transport is not significant
B,b	12.0	Cold vs warm storage is significant
C,c	23.9	“As received” vs dried, sieved is significant
D,d	97.3	100 mL vs 100 g is significant
E,e	61,000	0.1 g KCl vs 0.1 g $CaCl_2$ is significant
F,f	0.17	30-min vs 60-min equilibrium period is not significant
G,g	0.58	Not stirring vs stirring before testing is not significant

[1] Calculated as described in ASTM C1067 (2007); an *F* statistic ≥ 5.59 is significant at the 95% confidence level.

Table A-51 Alico Road Sand Ruggedness Study Results for Minimum Resistivity

Factors		Minimum Resistivity Determination							
Original	Change	1	2	3	4	5	6	7	8
A	a	CT	CT	CT	CT	WT	WT	WT	WT
B	b	CS	CS	WS	WS	CS	CS	WS	WS
C	c	wet	dry	wet	dry	wet	dry	wet	dry
D	d	DI	DI	DI-S	DI-S	DI-S	DI-S	DI	DI
E	e	SM	LG	SM	LG	LG	SM	LG	SM
F	f	1.0	1.5	1.5	1.0	1.0	1.5	1.5	1.0
G	g	no	yes	yes	no	yes	no	no	yes
Resistivity Results (ohm-cm)		8,800	9,500	7,750	12,500	11,000	9,950	11,000	9,050

A	Transport in cooler (~13°C) (CT)
a	Transport under ambient conditions (~27°C) (WT)
B	Store in refrigerator (~ 4°C) (CS)
b	Store at room temperature (~24°C) (WS)
C	Test "as received" (wet)
c	Dried at 60°C, No. 10 sieve (dry)
D	DI water (>1,000,000 ohm-cm; measured in large soil box) (DI)
d	DI water, sodium chloride added (150,000 ohm-cm, measured in small soil box) (DI-S)
E	Small soil box (SM)
e	Large soil box (LG)
F	1.0 kg soil (1.0)
f	1.5 kg soil (1.5)
G	No equilibrium period (no)
g	Equilibrium period of 30 min after adding 20% dilution water (yes)
Note 1	Sampling date was 11/12/2014; ruggedness study date was 11/23/2014
Note 2	4,000 ohm-cm conductivity standard was 4,150 ohm-cm at ~24.5°C

Table A-52 Alico Road Sand Significance of Ruggedness Study for Minimum Resistivity

Factors	Average	St Dev	Diff	*F*-tests	*t*-tests	Minimum Resistivity Was:
A	9,640	2,040				Higher if transported under ambient conditions; not significant
a	10,300	941	-613	0.236	0.605	
B	9,810	922				Higher if stored at room temperature; not significant
b	10,100	2,100	-263	0.210	0.826	
C	9,640	1,630				Higher if tested dried and sieved; not significant
c	10,300	1,540	-613	0.931	0.605	
D	9,600	985				Higher if tested with 150,000 ohm-cm water; not significant
d	10,300	2,000	-713	0.276	0.546	
E	8,890	905				Higher if tested in the large soil box; significant
e	11,000	1,230	-2,110	0.632	0.032	
F	10,340	1,750				Higher if tested with 1 kg of soil; not significant
f	9,550	1,360	788	0.687	0.503	
G	10,560	1,570				Higher for no equilibrium period; not significant
g	9,330	1,340	1,240	0.799	0.276	

Appendix B Treatment Study Results

Statistically-significant results are highlighted.

B.1 Mine 1 Wimauma Sand

Table B-1 Wimauma Sand Treatment Study Results for pH

Test Date	5/8/2014	5/9/2014	5/9/2014	5/10/2014	5/10/2014	5/15/2014
Treatment	1	2	3	4	5	6
Soil Slurry T, °C	28.5	23.0	23.0	23.3	23.3	25.0
Replicate 1	4.50	4.60	4.70	4.62	4.41	4.77
Replicate 2	4.57	4.67	4.68	4.71	4.63	4.79
Replicate 3	4.67	4.65	4.56	4.86	4.70	4.68
Avg	4.58	4.64	4.65	4.73	4.58	4.75
St Dev	0.09	0.04	0.08	0.12	0.15	0.06
t-tests		0.33	0.37	0.15	1.00	0.05
			0.90	0.29	0.54	0.05
				0.37	0.53	0.14
					0.25	0.84
						0.15
No *F*-tests were significant						
pH meter/electrode calibration for Accumet AP85/13-620-AP55						
Slope, %	Not recorded					
Offset, mV	Not recorded					
Treatments						
Treatment 1	On-site in the shade within 1 hr of sampling, and tested "as received"					
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), quartered, and tested “as received”					
Treatment 3	Sample was transported to the lab in a cooler (~15°C) and stored in the refrigerator (4 °C), brought to room temperature over several hr, quartered, and tested “as received”					
Treatment 4	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 85°C, sieved, mechanically split					
Treatment 5	Same as 4, except measurement was repeated after sample was quiescent at room temperature for an hr					
Treatment 6	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), soil was air-dried, sieved, mechanically split					

Table B-2 Wimauma Sand Treatment Study Results for Minimum Resistivity

Test Date	5/8/2014	5/9/2014	5/9/2014	5/10/2014	5/15/2014
Treatment	1	2	3	4	6
Soil Slurry T, °C	27.0	22.5	22.0	23.0	23.0
Replicate 1	39,000	42,500	42,000	48,500	50,000
Replicate 2	41,500	46,500	44,000	48,000	46,500
Replicate 3	45,000	42,000	44,000	44,000	46,500
Avg	41,800	43,700	43,300	46,800	47,700
St Dev	3,010	2,470	1,160	2,470	2,020
t-tests		0.46	0.47	0.09	0.05
			0.84	0.19	0.10
				0.09	0.03
					0.67
No *F*-tests were significant					
Resistivity meter calibration checks					
DI water, ohm-cm	310,000	850,000	850,000	1,100,000	Not recorded
Std, 4,000 ohm-cm	Not recorded	4,200	4,200	4,200	Not recorded
Treatment					
Treatment 1	On-site in the shade within 2 hr of sampling, and tested "as received"				
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), quartered, and tested “as received”				
Treatment 3	Sample was transported to the lab in a cooler (~15°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, and tested “as received”				
Treatment 4	Sample was transported to the lab at ambient temperature (~30°C and stored at ambient temperature (23-25°C), oven-dried at 85°C, sieved, mechanically split				
Treatment 5	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), soil was air-dried, sieved, mechanically split				

Table B-3 Wimauma Sand Treatment Study Results for Chloride

Test Date	6/1/2014	6/1/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Avg	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Results for chloride spike, ppm		
20 ppm spike	15	Not tested
10 ppm spike	Not tested	5
Treatments		
Treatment 1	Samples were transported cool, stored cold, quartered, oven-dried at 60°C, extracted with 100 g soil and 100 mL DI water and allowed to sit for 36 hr; samples were then filtered through a coarse, fast filter (Fisher, Q8); 50 mL of sample extract was diluted with 100 mL of DI water (3 x dilution).	
Treatment 2	Samples were transported cool, stored cold, quartered, oven-dried at 110°C, extracted with 100 g soil and 100 mL DI water and allowed to sit for 36 hr; samples were then filtered through a coarse, fast filter (Fisher, Q8); 50 mL of sample extract was diluted with 100 mL of DI water (3 x dilution).	
Notes		
Note 1	Analysis was with Hach chloride test kit, 5 to 400 mg/L	
Note 2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank	

Table B-4 Wimauma Sand Treatment Study Results for Sulfate

Test Date	6/1/2014	6/1/2014
Treatment	1	2
Replicate 1	12	9
Replicate 2	9	9
Replicate 3	9	12
Avg	10	10
St Dev	2	2
Results for sulfate check standard and spike, ppm		
20 ppm CS	17	Not tested
20 ppm spike	Not tested	21
Treatments		
Treatment 1	Samples were transported cool, stored cold, quartered, oven-dried at 60°C, extracted with 100 g soil and 100 mL DI water and allowed to sit for 36 hr; samples were then filtered through a coarse, fast filter (Fisher, Q8); 50 mL of sample extract was diluted with 100 mL of DI water (3 x dilution).	
Treatment 2	Samples were transported cool, stored cold, quartered, oven-dried at 110°C, extracted with 100 g soil and 100 mL DI water and allowed to sit for 36 hr; samples were then filtered through a coarse, fast filter (Fisher, Q8); 50 mL of sample extract was diluted with 100 mL of DI water (3 x dilution).	
Notes		
Note 1	Analysis was with Hach photometer test kit, 2 to 70 mg/L, on Range 1 (factory default)	

B.2 Mine 2 Jahna Sand

Table B-5 Jahna Sand Treatment Study Results for pH

Test Date	5/29/2014	5/30/2014	5/30/2014	6/5/2014	6/5/2014
Treatment	1	2	3	4	5
Avg Soil Slurry T, °C	27.1	23.3	23.1	23.7	23.7
Replicate 1	5.08	4.97	5.29	5.22	5.34
Replicate 2	5.08	4.76	5.00	5.35	5.37
Replicate 3	5.15	5.17	5.18	5.27	5.22
Average	5.10	4.97	5.16	5.28	5.31
St Dev	0.04	0.21	0.15	0.07	0.08
t-tests		0.32	0.58	0.02	0.02
			0.26	0.07	0.05
				0.25	0.19
					0.64
No *F*-tests were significant					
pH meter/electrode calibration for Accumet AP85/13-620-AP55					
Slope, %	Not recorded	94.3	97.7	Not recorded	Not recorded
Offset, mV	Not recorded	4.7	8.3	Not recorded	Not recorded
Treatments					
Treatment 1	On-site in the shade within 2 hr of sampling, soil "as received"				
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), quartered, and tested “as received”				
Treatment 3	Sample was transported to the lab in a cooler (~18°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, and tested “as received”				
Treatment 4	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60°C, sieved, mechanically split				
Treatment 5	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, sieved, mechanically split				

Table B-6 Jahna Sand Treatment Study Results for Minimum Resistivity

Test Date	5/29/2014	5/30/2014	5/30/2014	6/9/2014
Treatment	1	2	3	4
Soil Slurry T, °C	27.1	22.5	23.8	23.4
Replicate 1	110,000	125,000	120,000	110,000
Replicate 2	110,000	130,000	120,000	110,000
Replicate 3	100,000	120,000	120,000	115,000
Average	107,000	125,000	120,000	112,000
St Dev	5,770	5,000	0	2,890
t-tests		0.01	0.02	0.25
			0.16	0.02
				0.01
Standard deviation was significantly lower for treatment 3 than treatments 1, 2, and 4				
Resistivity meter calibration checks				
DI water, Ω-cm	Not recorded	1,100,000	1,100,000	850,000
Standard, 4000 Ω-cm	Not recorded	3,900	3,900	4,000
Treatments				
1	On-site in the shade within 2 hr of sampling, and tested "as received"			
2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), quartered, and tested "as received"			
3	Sample was transported to the lab in a cooler (~18°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, and tested "as received"			
4	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60°C, sieved, mechanically split			

Table B-7 Jahna Sand Treatment Study Results for Chloride

Test Date	6/1/2014	6/1/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Results for chloride spike, ppm		
20 ppm spike	15	Not tested
10 ppm spike	Not tested	5
Treatments		
Treatment 1	Sample was transported to the lab at ambient temperature (~30°C and stored at ambient temperature (23-25°C), oven-dried at 60°C, extracted with 1:1 soil:water, diluted x 3, filtered with 0.45 micron membrane filter	
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, extracted with 1:1 soil:water, diluted x 3, filtered with 0.45 micron membrane filter	
Notes		
Note 1	Analysis was with Hach chloride test kit, 5 to 400 mg/L	
Note 2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank	

Table B-8 Jahna Sand Treatment Study Results for Sulfate

Test Date	6/1/2014	6/1/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Results for sulfate check standard and spike, ppm		
20 ppm CS	17	Not tested
20 ppm spike	Not tested	21
Treatments		
Treatment 1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60°C, extracted with 1:1 soil:water, diluted x 3, filtered with 0.45 micron membrane filter	
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, extracted with 1:1 soil:water, diluted x 3, filtered with 0.45 micron membrane filter	
Notes		
Note 1	Analysis was with Hach photometer test kit, 2 to 70 mg/L, on Range 1 (factory default)	
Note 2	Photometer readings were 2 ppm or less (6 ppm as soil sulfate) and were below the method detection level	

B.3 Mine 3 Youngquist Sand

Table B-9 Youngquist Sand Treatment Study Results for pH

Test Date	6/19/2014	6/20/2014	6/20/2014	6/22/2014	7/11/2014
Treatment	1	2	3	4	5
Soil Slurry T, °C	28.2	21.2	21.0	21.1	24.8
Replicate 1	8.20	8.25	8.42	8.11	8.05
Replicate 2	8.17	8.33	8.44	8.16	8.20
Replicate 3	8.08	8.22	8.36	8.18	8.27
Average	8.15	8.27	8.41	8.15	8.24
St Dev	0.06	0.06	0.04	0.04	0.12
t-tests		0.07	0.00	1.00	0.77
			0.03	0.04	0.27
				0.00	0.03
					0.75
No *F*-tests were significant					
pH meter/electrode calibration for Accumet AP85/13-620-AP55					
Slope, %	95.0	97.9	97.9	97.9	98.5
Offset, mV	5.3	4.1	4.1	4.7	4.8
Treatments					
Treatment 1	On-site in the shade within 1 hr of sampling, and tested "as received"				
Treatment 2	Sample was transported to the lab at ambient temperature (~27-30°C) and stored at ambient temperature (22-24°C), quartered, and tested “as received”				
Treatment 3	Sample was transported to the lab in a cooler (~16-23°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, and tested “as received”				
Treatment 4	Sample was transported to the lab at ambient temperature (~27-30°C) and stored at ambient temperature (22-24°C), oven-dried at 60°C, sieved, mechanically split				
Treatment 5	Same as 4, except sample was dried at 110°C and tested with electrode/meter Accumet AB150/13-620-631				

Table B-10 Youngquist Sand Treatment Study Results for Minimum Resistivity

Test Date	6/19/2014	6/20/2014	6/20/2014	6/21/2014	6/22/2014
Treatment	1	2	3	4	5
Soil Slurry T, °C	29.2	22.0	21.1	22.0	21.4
Replicate 1	9,600	8,600	8,050	9,750	8,750
Replicate 2	10,200	9,200	7,850	10,500	8,650
Replicate 3	10,000	9,150	7,500	10,800	8,700
Average	9,930	8,980	7,800	10,300	8,700
St Dev	306	333	278	320	50
t-tests		0.02	0.00	0.31	0.00
			0.01	0.02	0.22
				0.00	0.01
					0.01
F-tests revealed a significantly lower variance for treatment 5 versus treatments 1, 2, and 4					
Resistivity meter calibration checks					
DI water, ohm-cm	Not recorded	>1,100,000	>1,100,000	Not recorded	>1,100,000
Std, 4 000 ohm-cm	Not recorded	4,400	5,050	Not recorded	4,400
Treatments					
Treatment 1	On-site in the shade within 2 hr of sampling, and tested "as received" (Note: terminals P1&C1 and P2&C2 were shorted)				
Treatment 2	Sample was transported to the lab at ambient temperature (~27-30 °C) and stored at ambient temperature (22-24 °C), quartered, and tested “as received”				
Treatment 3	Sample was transported to the lab in a cooler (~16-23 °C) and stored in the refrigerator (4 °C), brought to room temperature over several hr, quartered, and tested “as received”				
Treatment 4	Sample was transported to the lab at ambient temperature (~27-30 °C) and stored at ambient temperature (22-24 °C), quartered, and tested “as received” (Note: terminals P1&C1 and P2&C2 were shorted)				
Treatment 5	Sample was transported to the lab at ambient temperature (~27-30 °C) and stored at ambient temperature (22-24 °C), soil dried at 60 °C, sieved, mechanically split				

Table B-11 Youngquist Sand Treatment Study Results for Chloride

Test Date	7/10/2014	7/10/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Results for chloride check standard, ppm		
20 ppm CS	25	Not tested
Treatments		
Treatment 1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
Notes		
Note 1	Analysis was with Hach chloride test kit, 5 to 400 mg/L	
Note 2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank	

Table B-12 Youngquist Sand Treatment Study Results for Sulfate

Test Date	7/10/2014	7/10/2014
Treatment	1	2
Replicate 1	27	45
Replicate 2	36	36
Replicate 3	36	36
Average	33	39
St Dev	5	5
t-tests		0.23
Results for Sulfate Check Standard, ppm		
20 ppm CS	17	Not tested
Treatments		
Treatment 1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60 °C, extracted with 3:1 soil:water, filtered with Whatman 4, 4 drops conc HNO3 added, filtered with 0.45 micron membrane filter	
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 4, 4 drops conc HNO3 added, filtered with 0.45 micron membrane filter	
Notes		
Note 1	Analysis was with Hach photometer test kit, 2 to 70 mg/L, on Range 1 (factory default)	

B.4 Mine 4 Calhoun Sand

Table B-13 Calhoun Sand Treatment Study Results for pH

Test Date	7/14/2014	7/15/2014	7/15/2014
Treatment	1	2	3
Avg Soil Slurry T, C	31.5	23.5	24.0
Replicate 1	4.51	4.56	4.47
Replicate 2	4.72	4.60	4.59
Replicate 3	4.56	4.57	4.50
Replicate 4		4.53	
Replicate 5		4.74	
Replicate 6		4.56	
Average	4.60	4.59	4.52
St Dev	0.11	0.08	0.06
t-tests		0.77	0.35
			0.21
No *F*-tests were significant			
pH meter/electrode calibration for Accumet AP85/13-620-AP55			
Slope, %	98.6	99.1	96.6
Offset, mV	4.1	2.4	2.4
Treatments			
Treatment 1	On-site in the shade within 1 hr of sampling, and tested "as received"		
Treatment 2	Sample was transported to the lab at ambient temperature (~30-32°C) and stored at ambient temperature (~24°C), quartered, and tested "as received"		
Treatment 3	Sample was transported to the lab in a cooler (~17-23°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, and tested "as received"		

Table B-14 Calhoun Sand Treatment Study Results for Minimum Resistivity

Date	7/14/2014	7/15/2014	7/15/2014	7/16/2014
Treatment	1	2	3	4
Soil Slurry T, °C	32.4	22.6	24.1	23.5
Replicate 1	103,000	109,000	125,000	92,000
Replicate 2	85,000	110,000	120,000	97,000
Replicate 3	95,000	110,000	110,000	93,500
Average	94,300	110,000	118,000	94,200
St Dev	9,020	577	7,640	2,570
t-tests		0.04	0.02	0.98
			0.12	0.00
				0.01
Significant variance between treatment 2 and treatments 1 and 3				
Resistivity meter calibration checks				
DI water, ohm-cm	725,000	>1,000,000	>1,000,000	>1,000,000
	Treatments			
Treatment 1	On-site in the shade within 2 hr of sampling, and tested "as received"			
Treatment 2	Sample was transported to the lab at ambient temperature (~30-32°C) and stored at ambient temperature (~24°C), quartered, and tested "as received"			
Treatment 3	Sample was transported to the lab in a cooler (~17-23°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, and tested "as received"			
Treatment 4	Sample was transported to the lab at ambient temperature (~30-32°C) and stored at ambient temperature (~24°C), quartered, dried at 60°C, sieved through No. 10 sieve			

Table B-15 Calhoun Sand Treatment Study Results for Chloride

Test Date	7/18/2014	7/18/2014	7/18/2014
Treatment	1	2	3
Replicate 1	BD	BD	BD
Replicate 2	BD	BD	BD
Replicate 3	BD	BD	BD
Average	Not calculated	Not calculated	Not calculated
St Dev	Not calculated	Not calculated	Not calculated
Results for chloride check standard, ppm			
20 ppm CS	20	20	25
Treatments			
Treatment 1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter		
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter		
Treatment 3	Sample was transported to the lab in a cooler (~17-23°C) and stored in the refrigerator (4°C), quartered, oven-dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter		
Notes			
Note 1	Analysis was with Hach chloride test kit, 5 to 400 mg/L		
Note 2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank		

Table B-16 Calhoun Sand Treatment Study Results for Sulfate

Test Date	7/18/2014	7/18/2014	7/18/2014
Treatment	1	2	3
Replicate 1	BD	BD	9
Replicate 2	BD	9	BD
Replicate 3	BD	BD	BD
Average	Not calculated	Not calculated	Not calculated
St Dev	Not calculated	Not calculated	Not calculated
Treatments			
Treatment 1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter		
Treatment 2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven-dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter		
Treatment 3	Sample was transported to the lab in a cooler (~17-23°C) and stored in the refrigerator (4°C), quartered, oven-dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter		
Results for sulfate check standard, ppm			
20 ppm CS	13	16	16
Notes			
Note 1	Analysis was with Hach photometer test kit, 2 to 70 mg/L, on Range 1 (factory default)		
Note 2	Except for two extracts with photometer readings of 3 ppm (9 ppm as soil sulfate), photometer sulfate readings were 2 ppm or less (6 ppm as soil sulfate) and were below the method detection level		

B.5 Mine 5 Angelo’s Sand

Table C-17 Angelo’s Sand Treatment Study Results for pH

Test Date	9/17/2014	9/20/2014	9/20/2014	9/18/2014	9/18/2014
Treatment	1	2	3	4	5
Soil Slurry T, °C	23.5	24.6	24.3	24.5	24.5
Replicate 1	4.56	4.58	4.69	4.54	4.59
Replicate 2	4.55	4.57	4.58	4.56	4.60
Replicate 3	4.59	4.60	4.61	4.58	4.60
Average	4.57	4.58	4.63	4.56	4.60
St Dev	0.02	0.02	0.06	0.02	0.01
t-tests		0.33	0.16	0.71	0.07
			0.27	0.18	0.23
				0.13	0.41
					0.04
F-tests		0.70	0.24	0.96	0.14
			0.13	0.74	0.25
				0.22	0.02
					0.15
Meter/electrode Accumet AP85/13-620-AP55					
slope, %	97.3	.	.	.	97.0
offset, mV	9.5	.	.	.	10.6
buffer temp, C	24.1	.	.	.	24.5
Meter/electrode Accumet AB150/13-620-631					
slope, %	.	99.5	99.0	99.1	.
offset, mV	.	3.0	3.5	3.7	.
buffer temp, C	.	24.9	24.8	24.5	.
Treatments					
1	On-site testing, indoors				
2	Sample was transported to the lab at ambient temperature (~24°C) and stored at ambient temperature (~24°C), quartered, soil at "as received" moisture content				
3	Sample was transported in a cooler (~15-21°C) and stored in a refrigerator at 4°C, quartered, and brought to room temperature before testing "as received"				
4	Sample was transported to the lab at ambient temperature (~24°C) and stored at ambient temperature (~24°C), dried at 60°C, No. 10 sieve, mechanically split				
5	Sample was transported to the lab at ambient temperature (~24 °C) and stored at ambient temperature (~24°C), dried at 60°C, No. 10 sieve, mechanically split				

Table B-18 Angelo's Sand Treatment Study Results for Minimum Resistivity

Test Date	9/20/2014	9/20/2014	9/21/2014
Treatment	1	2	3
DI water, ohm-cm	780,000	780,000	1,000,000
Soil Slurry T, C	24.1	24.2	24.0
Replicate 1	17,000	19,000	17,500
Replicate 2	17,000	19,000	17,500
Replicate 3	17,000	19,500	17,000
Average	17,000	19,167	17,333
St Dev	0	289	289
t-tests		0.00	0.12
			0.00
F-tests		0.00	0.00
			1.00

Treatments	
1	Sample was transported to the lab at ambient temperature (~24°C) and stored at ambient temperature (~24°C), quartered, soil at "as received" moisture content
2	Sample was transported in a cooler (~15-21°C) and stored in a refrigerator at 4°C, quartered, and brought to room temperature before testing at "as received" moisture content
3	Sample was transported to the lab at ambient temperature (~24°C) and stored at ambient temperature (~24°C), dried at 60°C, No. 10 sieve, mechanically split

Table B-19 Angelo's Sand Treatment Study Results for Chloride

Test Date	9/19/2014	9/19/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Results for chloride spike, ppm		
30 ppm CS	35	Not tested
Treatments		
1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
Notes		
1	Analysis was with Hach chloride test kit, 5 to 400 mg/L	
2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank	

Table B-20Angelo's Sand Treatment Study Results for Sulfate

Test Date	9/19/2014	9/19/2014	9/19/2014	9/19/2014
Treatment	1	2	3	4
Test Range	Range 1	Range 2	Range 1	Range 2
Replicate 1	24	27	21	27
Replicate 2	27	33	21	27
Replicate 3	21	21	18	24
Average	24	27	20	26
St Dev	3	6	2	2
t-tests		0.48	0.12	0.37
			0.12	0.80
				0.01
F-tests		0.40	0.50	0.50
			0.15	0.15
				1.00
Treatments				
1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter			
2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter			
3	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter			
4	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter			
	Range 1		Range 2	
30 ppm CS	31		40	
Notes				
1	Analysis was with photometer test kit, 2 to 70 mg/L, on range 1 (factory default)			
2	Except for two extracts with photometer readings of 3 ppm (9 ppm in soil), photometer readings were 2 ppm or less and were below the method detection level			

B.6 Mine 6 Sebring Sand

Table B-21 Sebring Sand Treatment Study Results for pH

Test Date	10/15/2014	10/16/2014	10/17/2014	10/20/2014	10/16/2014	10/17/2014
Treatment	1	2	3	4	5	6
Soil Slurry T, °C	25.8	24.5	24.7	24.5	24.1	24.8
Replicate 1	4.37	4.27	4.39	4.35	4.29	4.43
Replicate 2	4.43	4.33	4.42	4.39	4.33	4.46
Replicate 3	4.30	4.33	4.43	4.43	4.36	4.47
Average	4.37	4.31	4.41	4.39	4.33	4.45
St Dev	0.07	0.03	0.02	0.04	0.04	0.02
t-tests		0.25	0.30	0.62	0.40	0.09
			0.01	0.06	0.59	0.00
				0.42	0.02	0.08
					0.11	0.07
						0.01
No *F*-tests were significant						
Meter/electrode Accumet AP85/13-620-AP55						
slope, %	95.4	.	.	.	95.0	96.2
offset, mV	1.8	.	.	.	2.4	4.7
buffer, C	25.7	.	.	.	24.5	24.6
Meter/electrode Accumet AB150/13-620-631						
slope, %	.	99.7	99.0	99.2	.	.
offset, mV	.	2.1	1.3	2.30	.	.
buffer, C	.	24.6	25.0	25.1	.	.
Treatments						
1	On-site in the shade within 2 hr of sampling, soil "as received"					
2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (~25°C), quartered, soil tested "as received"					
3	Sample was transported to the lab in a cooler (~9-19°C) and stored in the refrigerator (4°C), brought to room temperature, quartered, soil tested "as received"					
4	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (~24°C), dried at 60°C for ~4 hr, sieved through a No. 10 mesh, and mechanically split					
5	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (~24°C), quartered, soil tested "as received"					
6	Sample was transported to the lab in a cooler (~9-19°C) and stored in the refrigerator (4°C), brought to room temperature, quartered, soil tested "as received"					

Table B-22 Sebring Sand Treatment Study Results for Minimum Resistivity

Test Date	10/16/2014	10/17/2014	10/19/2014
Treatment	1	2	3
DI water, ohm-cm	>1,000,000	>1,000,000	810,000
Conductivity Std, 4,000 ohm-cm	4,000	.	4,000
Soil Slurry T, C	24.0	24.3	24.8
Replicate 1	40,000	36,000	32,000
Replicate 2	38,000	38,500	30,500
Replicate 3	40,000	38,000	31,500
Average	39,300	37,500	31,300
St Dev	1,160	1,320	764
t-tests		0.14	0.00
			0.00
F-tests		0.86	0.61
			0.50
Treatments			
1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (~25°C), quartered, soil tested at the "as received" moisture content		
2	Sample was transported to the lab in a cooler (~9-19°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, soil was tested at "as received" moisture content		
3	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (~25°C), dried at 60°C for ~ 4 hr, sieved through a No. 10 mesh, and mechanically split		

Table B-23 Sebring Sand Treatment Study Results for Chloride

Test Date	10/19/2014	10/19/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Results for Chloride Check Standard, ppm		
30 ppm CS	30	
Treatments		
1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
Notes		
1	Analysis was with Hach chloride test kit, 5 to 400 mg/L	
2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank	

Table B-24 Sebring Sand Treatment Study Results for Sulfate

Test Date	10/19/2014	10/19/2014
Treatment	1	2
Replicate 1	12	21
Replicate 2	12	24
Replicate 3	12	15
Average	12	20
St Dev	0	4
t-test		0.04
F-test		0.00
Treatments		
1	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
2	Sample was transported to the lab at ambient temperature (~30°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Fisher Q8, filtered with 0.45 micron membrane filter	
Results for Sulfate Check Standard, ppm		
30 ppm CS	34	
Notes		
1	Analysis was with photometer test kit, 2 to 70 mg/L, on range 1 (factory default); reagent lot was 4120	
2	Except for two extracts with photometer readings of 3 ppm (9 ppm in soil), photometer readings were 2 ppm or less and were below the method detection level	

B.7 Mine 7 Clermont Sand

Table B-25 Clermont Sand Treatment Study Results for pH

Test Date	10/29/2014	11/1/2014	11/1/2014	11/1/2014	11/1/2014	11/2/2014
Treatment	1	2	3	4	5	6
Soil Slurry T, °C	28.5	23.5	23.4	23.3	23.0	23.4
Replicate 1	7.55	7.30	7.44	7.54	7.49	7.69
Replicate 2	7.57	7.28	7.80	7.39	7.46	7.93
Replicate 3	7.56	7.48	7.45	7.39	7.65	7.69
Average	7.56	7.35	7.56	7.44	7.53	7.77
St Dev	0.01	0.11	0.21	0.09	0.10	0.14
t-tests		0.03	0.98	0.08	0.68	0.06
			0.19	0.34	0.11	0.02
				0.39	0.83	0.22
					0.29	0.02
						0.08
F-tests		0.02	0.00	0.03	0.02	0.01
			0.45	0.76	0.92	0.77
				0.30	0.40	0.63
					0.84	0.56
						0.70
Meter/electrode Accumet AP85/13-620-AP55						
slope, %	97.7	.	.		95.0	96.9
offset, mV	1.2	.	.		2.4	7.7
buffer, C	28.0	.	.		24.5	23.3
Meter/electrode Accumet AB150/13-620-631						
slope, %	.	99.7	99.7	99.6	.	
offset, mV	.	2.0	2.0	1.70	.	
buffer, C	.	23.5	23.5	23.7	.	
Treatments (Note: 0.1 g KCl was added to 100 g soil)						
1	On-site in the shade within 2 hr of sampling, soil "as received" moisture content					
2	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (~24°C), quartered, soil tested at the "as received" moisture content					
3	Sample was transported to the lab in a cooler (~8-19°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, soil was tested at "as received"					
4	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (~24°C), dried at 60°C for ~4 hr, sieved through a No. 10 mesh, and mechanically split					
5	Sample was transported to the lab at ambient temperature (~28 °C) and stored at ambient temperature (~24°C), quartered, soil tested at the "as received" moisture content					
6	Sample was transported to the lab in a cooler (~8-19°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, soil was tested at "as received" moisture content					

Table B-26 Clermont Sand Treatment Study Results for Minimum Resistivity

Test Date	11/1/2014	11/1/2014	11/3/2014
Treatment	1	2	3
DI water, ohm-cm	>1,000,000	.	930,000
Conductivity Std, 4,000 ohm-cm	4,100	.	4,200
Soil Slurry T, °C	21.3	22.4	22.4
Replicate 1	33,000	24,000	26,500
Replicate 2	33,000	25,500	27,500
Replicate 3	32,000	24,000	28,000
Average	32,700	24,500	27,300
St Dev	577	866	764
t-tests		0.00	0.00
			0.01
F-tests		0.62	0.73
			0.88
Treatments			
1	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (~24°C), quartered, soil tested at the "as received" moisture content		
2	Sample was transported to the lab in a cooler (~8-19°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, soil was tested at "as received" moisture content		
3	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (~24°C), dried at 60°C for ~4 hr, sieved through a No. 10 mesh, and mechanically split		

Table B-27 Clermont Sand Treatment Study Results for Chloride

Test Date	11/3/2014	11/3/2014	11/3/2014	11/3/2014
Treatment	1	2	3	4
Replicate 1	BD	BD	BD	BD
Replicate 2	BD	BD	BD	BD
Replicate 3	BD	BD	BD	BD
Average	Not calculated	Not calculated	Not calculated	Not calculated
St Dev	Not calculated	Not calculated	Not calculated	Not calculated
Chloride concentrations were below method detection (BD) level				
Treatments				
1	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
2	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
3	Sample was transported to the lab in a cooler (8-19°C) and stored in a refrigerator (4°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
4	Sample was transported to the lab in a cooler 8-19°C) and stored in a refrigerator (4°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
Results of Chloride Check Standard, ppm				
30 ppm CS	30			
Notes				
1	Analysis was with chloride test kit, 5 to 400 mg/L			
2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank			

Table B-28 Clermont Sand Treatment Study Results for Sulfate

Test Date	11/3/2014	11/3/2014	11/3/2014	11/3/2014
Treatment	1	2	3	4
Replicate 1	BD	BD	BD	BD
Replicate 2	BD	BD	BD	BD
Replicate 3	BD	BD	BD	BD
Average	Not calculated	Not calculated	Not calculated	Not calculated
St Dev	Not calculated	Not calculated	Not calculated	Not calculated
Sulfate concentrations were below method detection (BD) level				
Treatments				
1	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
2	Sample was transported to the lab at ambient temperature (~28°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
3	Sample was transported to the lab in a cooler (8-19°C) and stored in a refrigerator (4°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
4	Sample was transported to the lab in a cooler 8-19°C) and stored in a refrigerator (4°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 4, filtered with 0.45 micron membrane filter			
Results of Sulfate Check Standard, ppm				
30 ppm CS	36			
Notes				
1	Analysis was with photometer test kit, 2 to 70 mg/L, on range 1 (factory default); reagent lot was 4120			
2	Except for two extracts with photometer readings of 3 ppm (9 ppm in soil), photometer readings were 2 ppm or less and were below the method detection level			

B.8 Mine 8 Alico Road Sand

Table B-29 Alico Road Sand Treatment Study Results for pH

Test Date	11/12/2014	11/15/2014	11/15/2014	11/15/2014	11/15/2014	11/16/2014
Treatment	1	2	3	4	5	6
Slurry T, °C	22.4	23.7	23.7	23.4	23.4	24.4
Replicate 1	8.93	9.02	8.96	8.91	9.04	8.95
Replicate 2	8.98	9.06	9.04	8.98	9.06	9.02
Replicate 3	9.05	8.99	8.98	8.88	9.01	8.98
Average	8.99	9.02	8.99	8.92	9.04	8.98
Std Dev	0.06	0.04	0.04	0.05	0.03	0.04
t-tests		0.41	0.88	0.24	0.26	0.94
			0.39	0.05	0.62	0.24
				0.14	0.20	0.77
					0.03	0.17
						0.10
F-tests	No *F*-tests were significant					
Meter/electrode Accumet AP85/13-620-AP55						
slope, %	95.0	.	.	.	97.9	98.6
offset, mV	0	.	.	.	3.5	3.5
buffer, C	22.7	.	.	.	23.4	23.4
Meter/electrode Accumet AB150/13-620-631						
slope, %	.	99.1	99.1	99.5	.	.
offset, mV	.	1.9	1.9	3.50	.	.
buffer, C	.	24.1	24.1	24.4	.	.

Treatments (Note: 0.1 g KCl added per 100 g sample)	
1	On-site in the shade within 2 hr of sampling, soil "as received"
2	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (~24°C), quartered, soil tested "as received"
3	Sample was transported to the lab in a cooler (~19-20°C) and stored in the refrigerator (4°C), brought to room temperature, quartered, soil tested "as received"
4	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (~24°C), dried at 60°C for ~4 hr, and sieved through a No. 10 mesh
5	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (~24°C), quartered, soil tested "as received"
6	Sample was transported to the lab in a cooler (~19-20°C) and stored in the refrigerator (4°C), brought to room temperature, quartered, soil tested "as received"

Table B-30 Alico Road Sand Treatment Study Results for Minimum Resistivity

Test Date	11/15/2014	11/15/2014	11/16/2014
Treatment	1	2	3
DI water, ohm-cm	>1,000,000	.	>1,000,000
Conductivity Std, 4,000 ohm-cm	4,200	.	.
Soil Slurry T, °C	22.4	23.6	23.8
Replicate 1	11,000	11,500	11,000
Replicate 2	11,000	12,000	11,000
Replicate 3	11,000	11,500	10,500
Avg	11,000	11,700	10,800
St Dev	0	289	289
t-tests		0.02	0.37
			0.02
F-tests		0.00	0.00
			1.00

Treatments	
1	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (~24°C), quartered, soil tested at the "as received" moisture content
2	Sample was transported to the lab in a cooler (~19-20°C) and stored in the refrigerator (4°C), brought to room temperature over several hr, quartered, soil was tested at "as received" moisture content
3	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (~24°C), dried at 60°C for 4 hr, and sieved through a No. 10 mesh

Table B-31 Alico Road Sand Treatment Study Results for Chloride

Test Date	11/18/2014	11/18/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	15	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
30 ppm CS	35	.
Treatments		
Treatment 1	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 41, filtered with 0.45 micron membrane filter	
Treatment 2	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 41, filtered with 0.45 micron membrane filter	
Notes		
Note 1	Analysis was with Hach chloride test kit, 5 to 400 mg/L	
Note 2	Samples turned color with one drop of silver nitrate reagent, indicating that the concentration was at or below the minimum detection level of 5 ppm; less if corrected for the blank	

Table B-32 Alico Road Sand Treatment Study Results for Sulfate

Test Date	11/18/2014	11/18/2014
Treatment	1	2
Replicate 1	BD	BD
Replicate 2	BD	BD
Replicate 3	BD	BD
Average	Not calculated	Not calculated
St Dev	Not calculated	Not calculated
Treatments		
Treatment 1	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (23-25°C), oven dried at 60°C, extracted with 3:1 soil:water, filtered with Whatman 41, filtered with 0.45 micron membrane filter	
Treatment 2	Sample was transported to the lab at ambient temperature (~29°C) and stored at ambient temperature (23-25°C), oven dried at 110°C, extracted with 3:1 soil:water, filtered with Whatman 41, filtered with 0.45 micron membrane filter	
Results for sulfate check standard, ppm		
30 ppm CS	33	
Notes		
Note 1	Analysis was with Hach photometer test kit, 2 to 70 mg/L, on Range 1 (factory default)	
Note 2	Except for two extracts with photometer readings of 3 ppm (9 ppm as soil sulfate), photometer sulfate readings were 2 ppm or less (6 ppm as soil sulfate) and were below the method detection level	

B.9 ANOVA All Sands

B.9.1 ANOVA for pH—all sands

Table B-33 Input Data for pH ANOVA

Mine	1	2	3	4	5	6	7	8
Replicate 1	4.70	5.29	8.42	4.47	4.54	4.35	7.54	8.95
Replicate 2	4.68	5.00	8.44	4.59	4.56	4.39	7.39	9.02
Replicate 3	4.56	5.18	8.36	4.50	4.58	4.43	7.39	8.98

Note: For each soil, treatment selected for table was matched with treatment for replicate study samples.

Table B-34 Treatment Study ANOVA for pH

ANOVA: Single Factor for pH

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Mine 1	3	13.94	4.65	0.0057
Mine 2	3	15.47	5.16	0.0214
Mine 3	3	25.22	8.41	0.0017
Mine 4	3	13.56	4.52	0.0039
Mine 5	3	13.68	4.56	0.0004
Mine 6	3	13.17	4.39	0.0016
Mine 7	3	22.32	7.44	0.0075
Mine 8	3	26.95	8.98	0.0012

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	78.49	7	11.21	2,060	2.01E-22	2.66
Within Groups	0.09	16	0.01			
Total	78.58	23				

B.9.2 ANOVA for minimum resistivity—mines 5-8

Table B-35 ANOVA Input Data for Minimum Resistivity (ohm-cm)

Mine 5	Mine 6	Mine 7	Mine 8
17,500	32,000	26,500	11,000
17,500	30,500	27,500	11,000
17,000	31,500	28,000	10,500

Note: For each soil, treatment selected for table was matched with treatment for replicate study samples.

Table B-36 Treatment Study ANOVA for Minimum Resistivity (ohm-cm)

ANOVA: Single Factor for Minimum Resistivity

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Mine 5	3	52,000	17,300	83,300
Mine 6	3	94,000	31,300	583,000
Mine 7	3	82,000	27,300	583,000
Mine 8	3	32,500	10,800	83,300

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	7.85E+08	3	2.62E+08	785	3.23E-10	4.07
Within Groups	2,670,000	8	333,300			
Total	7.88E+08	11				

B.9.3 ANOVA for sulfate—mines 1, 3, 5, and 6

Table B-37 ANOVA Input Data for Sulfate (ppm)

Replicate	Mine 1	Mine 3	Mine 5	Mine 6
1	12	27	24	12
2	9	36	27	12
3	9	36	21	12

Table B-38 Treatment Study ANOVA for Sulfate (ppm)

ANOVA: Single Factor for Sulfate

SUMMARY

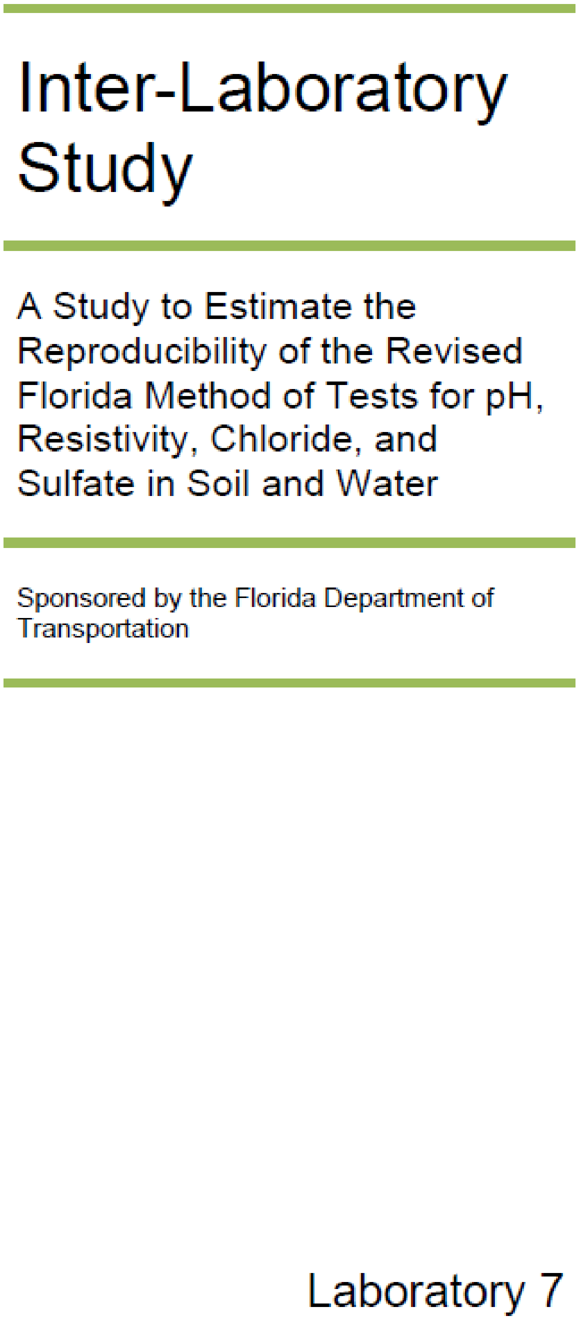
Groups	*Count*	*Sum*	*Average*	*Variance*
Mine 1	3	30	10	3
Mine 3	3	99	33	27
Mine 5	3	72	24	9
Mine 6	3	36	12	0

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	1050	3	349	36	5.54E-05	4.07
Within Groups	78	8	10			
Total	1120	11				

Appendix C Inter-Laboratory Study Plan and Data Sheet

C.1 First Inter-Laboratory Study



Inter-Laboratory Study

A Study to Estimate the Reproducibility of the Revised Florida Method of Tests for pH, Resistivity, Chloride, and Sulfate in Soil and Water

Sponsored by the Florida Department of Transportation

Laboratory 7

FDOT Inter-Laboratory Study Contact:

Noreen Poor, Ph. D., P. E.

Associate Research Professor
University of South Florida
Department of Civil & Environmental Engineering
4202 E. Fowler Avenue
Tampa, Florida 32905
(813) 956-0855 Cell
npoor@usf.edu
Hr: M-F 9:00 a.m. - 5:30 p.m.

Study Start Date: Tuesday, January 6, 2015
Study End Date: Thursday, January 8, 2015

Participant Instructions

1. Background

   Florida Department of Transportation (FDOT) has prepared revisions to the Florida Method of Tests (FMs) for Determining pH in Soil and Water (FM 5-550), Resistivity in Soil and Water (FM 5-551), Chloride in Soil and Water (FM 5-552), and Sulfate in Soil and Water (FM 5-553); revised methods are provided in Attachments A, B, C, and D, respectively. These revisions update and expand the methods' procedural details and include significant changes to method equipment, sample processing, and data management.

2. Scope and Purpose of Study

   The purpose of this study is to estimate a multi-laboratory precision (reproducibility) for the revised methods and to the extent practicable is designed in accordance with ASTM C802.[1]

   Over a three-day period, each participating laboratory will analyze in two select backfill (FDOT 092L) materials for pH, resistivity, chloride, and sulfate per the revised FMs. Results for each material will be aggregated to produce an estimates of within-laboratory and between-laboratory variances and, consistent with ASTM C670,[2] a precision statement to accompany each of the revised methods.

3. Revised Methods

   Results of field testing and laboratory analyses suggested that the accuracy and precision of the Florida Methods (FMs) for pH, resistivity, chloride, and sulfate could be improved with relatively small changes in method procedures. Changes to the FMs belong in one of five categories: (1) minor edits to method grammar, organization, and units of measure; (2) updates to the apparatus and reagents sections, with a hazardous materials note as appropriate; (3) step-by-step instructions to facilitate method oversight; (4) one or more quality assurance/quality control procedures; and (5) a new section for method precision and bias, to be completed as part of this inter-laboratory study.

   Materials provided have been dried at 60°C, sieved through a No. 10 (2 mm) mesh, and mechanically split into ~1,500-g samples. Chloride and sulfate has been added by mechanical mixer to one of the two materials to assure that these quantities are above the method detection levels.

   a. FM for the Determination of pH in Soil and Water

Revisions were made to the scope, apparatus, reagent, samples, sample preparation, and test procedure sections of the FM. Refer to Attachment A for the revised method. Based on ruggedness and other factor analysis studies as well as laboratory visits, major sources of variability in the FM were

- Measurement temperature,
- Electrode condition, and
- Ionic strength of the soil solution.

A pH meter with automatic temperature compensation (ATC) measures the sample temperature and corrects the slope of the calibration curve for the measurement temperature. Ideally, the buffers and the samples are at 25°C, but with ATC, buffers and samples need only to be at or near the same temperature. This is especially important if ambient temperatures are more than a few °C from standard temperature. The revised method requires a pH/mV meter with ATC and equipped with a 3-in-1 combination electrode.

The pH meter combination electrode is a delicate and sensitive sensor and with routine treatment and use its lifetime is ~18 months. A 3-in-1 combination electrode typically encases a glass-bulb indicating electrode, a silver/silver chloride reference electrode, and a thermocouple. Attention to electrode performance is critical to a precise and accurate pH measurement. Over time and with use the reference electrode is consumed, but temporary or permanent damage to the electrode can be caused by contamination or depletion of the filling solution, scratches or cracks on the glass bulb surface, and clogging of the liquid junction, as examples. Electrode condition can be monitored through calibration and performance checks, which are included in the revised FM.

For pH measurement in low-ionic strength (low salt content) a stable pH reading can take 5 minutes or more to obtain, as the reading is affected by the exchange of carbon dioxide between the sample and the atmosphere, the effects of stirring and vibrations, and a mismatch between the ionic strength of the sample and the reference solution in the electrode.

b. FM of Test for Resistivity in Soil and Water

Revisions were made to the scope, apparatus, reagent, samples, sample preparation, and test procedure sections of the FM. Refer to Attachment B for the revised method. Based on ruggedness and other factor analysis studies as well as laboratory visits, major sources of variability in the FM were

- Measurement temperature, and
- Water content of soil slurry placed in the soil box during resistivity testing.

Resistivity measurements are sensitive to temperature. The revised FM requires that samples be brought to room temperature and that the soil slurry temperature be measured and recorded.

ASTM G187[3] and AASHTO T288[4] represent two different positions along the soil resistivity continuum: ASTM G187 measures soil resistivity when the soil is just saturated and AASHTO T288 measures minimum soil resistivity, where the water from soil slurry is decanted into the soil box and tested as the water content in the slurry increases. The revised FM adopts the approach of AASHTO T288 for obtaining a minimum resistivity.

ASTM D1193[5] Type 4 reagent water, with a lower resistivity bound of 200,000 ohm-cm is recommended for resistivity measurements. The revised FM recommends as a best practice a daily check of dilution water resistivity because on-site water treatment systems can experience break-through of ions and bottled water can over time absorb ions from acidic and basic gases in the atmosphere. A higher ion concentration in dilution water translates into a lower resistivity.

The revised method also recommends that the resistivity meter calibration be checked at least once per quarter with a National Institute of Standards and Technology (NIST)-traceable conductivity standard.

c. FM of Test for Chloride in Soil and Water

Revisions were made to the scope, apparatus, reagents, samples, sample preparation, and test procedure sections of the FM. Refer to Attachment C for a revised method. The FM offers a choice of one of two methods: (1) a Hach chloride test kit (or equivalent) as a laboratory-based screening approach, or (2) for a greater degree of accuracy and precision an analytical approach as described by the Standard Method for the Evaluation of Water and Wastewater 4500-Cl^- or 4110 B.[6] Based on ruggedness and other factor analysis studies as well as laboratory visits major sources of variability in the FM were:

- Soil mass,
- Suspended solids or color in the filtered sample extract,
- Reagent quality, and

- Blank correction.

For chloride determination an accurate soil mass can be obtained if the soil is dried to a constant mass and its mass weighed on an analytical balance; these two requirements limit the portability of the method. Residual suspended solids or color, if present, can be removed by vacuum filtration of the extract through a 0.45-micron filter as a final treatment step. For some soils, ferric sulfate addition may be required to settle suspended particles prior to filtration. A separate 3:1 water-to-soil extract is prepared for chloride and sulfate, so that if needed ferric sulfate can be added to the unfiltered extract. A chloride check standard and an associated reagent blank help to establish the sample color at the titration endpoint, to guard against bad reagents and to subtract out any chloride contamination in the glassware and dilution water.

d. FM of Test for Sulfate in Soil and Water

Revisions were made to the scope, apparatus, reagents, samples, sample preparation, and test procedure sections of the FM. Refer to Attachment D for a revised method. The FM offers a choice of one of two methods: (1) a Hach sulfate photometer test kit (or equivalent) as a laboratory-based screening approach, or (2) for a greater degree of accuracy and precision an analytical approach as described by the Standard Method for the Evaluation of Water and Wastewater 4500-SO_4^{2-} or 4110 B.[6] Based on ruggedness and other factor analysis studies as well as laboratory visits major sources of variability in the FM were:

- Soil mass,
- Suspended solids or color in the filtered sample extract,
- Reagent quality, and
- Sulfate calibration curve.

For sulfate determination an accurate soil mass can be obtained if the soil is dried to a constant mass and its mass weighed on an analytical balance; these two requirements limit the portability of the method. Residual suspended solids or color, if present, can be removed by vacuum filtration of the extract through a 0.45-micron filter as a final treatment step. For some soils, acid addition may be required to settle suspended particles prior to filtration. A separate 3:1 water-to-soil extract is prepared for chloride and sulfate, so that if needed hydrochloric acid can be added to the unfiltered extract. A photometer with factory-programmed sulfate calibration curves give reasonable results provided the curve is periodically checked, as the potency of the reagents used in the method varies by lot number and possibly with the age of the reagents. A sulfate check standard and associated reagent blank help to guard against bad reagents, contamination of dilution water, or a mismatch between reagent and photometer response.

4. Sample management

   Each participating laboratory will receive a 1,500-g sample of air-dried and sieved soil of each material, which is sufficient soil for each FM to be run once. Samples will be delivered to participating laboratories with one month of the study start date.

5. Data management

   Data should be handled and reported as required by the revised FMs. Measurements that are below detection should be flagged as such. Upon completion of testing, scan and submit the attached data sheet (Attachment E) electronically to the study contact. Keep data records on file for at least one year past the study date.

References

1. ASTM C802-2009a Standard Practice for Conducting an Inter-Laboratory Test Program to Determine the Precision of Test Methods for Construction Materials. ASTM International, West Conshohocken, Pennsylvania. 18 pp.

2. ASTM C670-2003 Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials, ASTM International, West Conshohocken, Pennsylvania. 9 pp.

3. ASTM G187-2012a. Standard Test Method for Measurement of Soil Resistivity Using the Two-Electrode Soil Box Method G 187-2012a. ASTM International, West Conshohocken, Pennsylvania. 6 pp.

4. AASHTO T288-2012. Standard Method of Test for Determining Minimum Laboratory Soil Resistivity. American Association of State Highway and Transportation Officials, Washington, D. C. 7 pp.

5. ASTM D1193-2006. Standard Specification for Reagent Water. ASTM International, West Conshohocken, Pennsylvania. 5 pp.

6. Rice, E. W., Baird, R. B., Easton, A. D., Clesceri, L. S., Editors, 2012. *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition, American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF), APHA Publication Office, Washington, D. C.

Attachment A Revised FM5-550
Attachment B Revised FM5-551

Attachment C Revised FM5-552
Attachment D Revised FM5-553
Attachment E Inter-Laboratory Study Data Sheet

Data Sheet

Select Backfill (092L)

Complete and submit data sheet by e-mail to npoor@usf.edu on or before January 9, 2015.

Sample	pH, pH units	Solution Temperature, °C
Example	pH 7.01	25.0
Material A		
Material B		

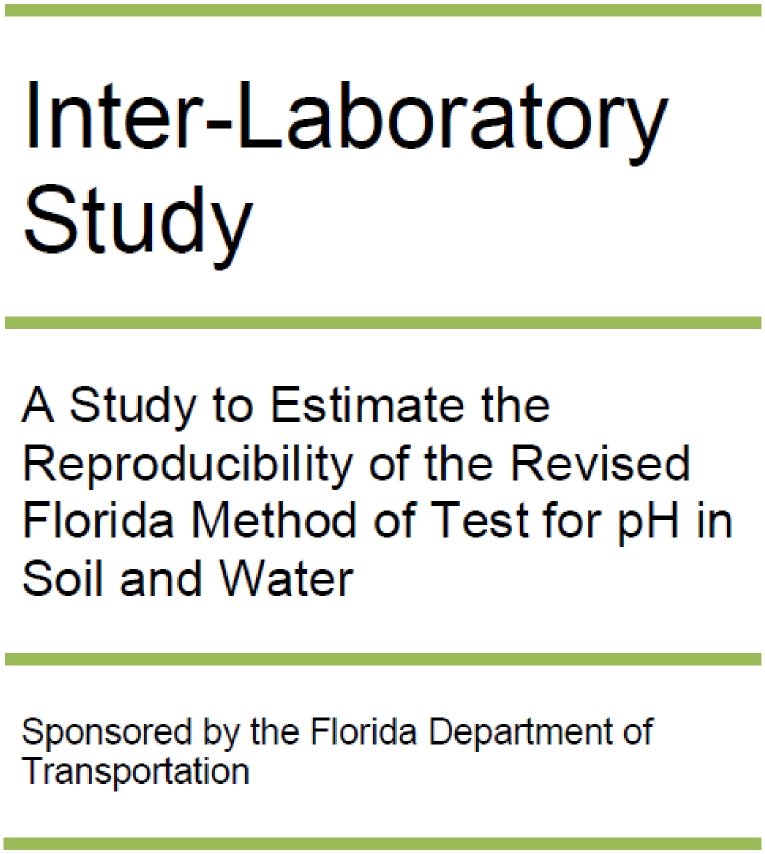
Sample	Minimum Resistivity, ohm-cm	Solution Temperature, °C
Example	19,500	25.0
Material A		
Material B		

Sample	Soil Chloride Concentration, ppm
Example	35
Material A	
Material B	

Sample	Soil Sulfate Concentration, ppm
Example	6 (Below detection)
Material A	
Material B	

Comments (type or print legibly):

C.2 Second Inter-Laboratory Study



Inter-Laboratory Study

A Study to Estimate the Reproducibility of the Revised Florida Method of Test for pH in Soil and Water

Sponsored by the Florida Department of
Transportation

FDOT Inter-Laboratory Study Contact:

Noreen Poor, Ph. D., P. E.

Associate Research Professor
University of South Florida
Department of Civil & Environmental Engineering
4202 E. Fowler Avenue
Tampa, Florida 32905
(813) 956-0855 Cell
npoor@usf.edu
Hr: M-F 9:00 a.m. - 5:30 p.m.

Study Start Date: Wednesday, March 11, 2015
Study End Date: Thursday, March 12, 2015

Participant Instructions

1. Background

Florida Department of Transportation (FDOT) has prepared proposed revisions to the Florida Method of Test (FM) for Determining pH in Soil and Water (FM 5-550) (attached). These revisions update and expand the method's procedural details and include changes to method equipment, sample processing, and data management.

2. Scope and Purpose of Study

The purpose of this study is to estimate a multi-laboratory precision (reproducibility) for the revised method and to the extent practicable the study is designed in accordance with ASTM C802.[1]

Over a two-day period, each participating laboratory will analyze in duplicate two select backfill (FDOT 092L) materials for pH. These materials are labeled Material C and Material D. Results for each material will be aggregated to produce an estimate of within-laboratory and between-laboratory variance and, consistent with ASTM C670,[2] a precision statement to accompany the revised method.

3. Revised Method

Results of field testing and laboratory analyses suggested that the accuracy and precision of the Florida Method (FM) for pH could be improved with relatively small changes in method procedures. Changes to the FM belong in one of five categories: (1) minor edits to method grammar, organization, and units of measure; (2) updates to the apparatus and reagents sections; (3) step-by-step instructions to facilitate method oversight; (4) one or more quality assurance/quality control procedures; and (5) a new section for method precision and bias, to be completed as part of this inter-laboratory study.

Materials provided have been dried at 60°C, sieved through a No. 10 (2 mm) mesh, and mechanically split into ~200-g (Material D) and ~300-g (Material C) samples.

FM for the Determination of pH in Soil and Water

Revisions were made to the scope, apparatus, reagent, samples, sample preparation, and test procedure sections of the FM (see attached method).

Based on ruggedness and other factor analysis studies as well as laboratory visits and an inter-laboratory study, major sources of variability in the FM were

- Measurement temperature,
- Electrode condition,
- Electrode memory, and
- Ionic strength of the soil solution.

A pH meter with automatic temperature compensation (ATC) measures the sample temperature and corrects the slope of the calibration curve for the measurement temperature. Ideally, the buffers and the samples are at 25°C, but with ATC, buffers and samples need only to be at or near the same temperature. This is especially important if ambient temperatures are more than a few °C from standard temperature. The revised method requires a pH/mV meter with ATC and equipped with a 3-in-1 combination electrode.

The pH meter combination electrode is a delicate and sensitive sensor and with routine treatment and use its lifetime is ~18 months. A 3-in-1 combination electrode typically encases a glass-bulb indicating electrode, a silver/silver chloride reference electrode, and a thermocouple. Attention to electrode performance is critical to a precise and accurate pH measurement. Over time and with use the reference electrode is consumed, but temporary or permanent damage to the electrode can be caused by contamination or depletion of the filling solution, scratches or cracks on the glass bulb surface, and clogging of the liquid junction, as examples. Electrode condition can be monitored through calibration and performance checks, which are included in the revised FM.

The electrode has a memory of its previous measurement and the contribution of this memory on the current pH measurement is more pronounced for low-ionic strength (low salt content) solutions. The memory effect on sample pH can be reduced by careful attention to rinsing and drying the electrode between measurements and by a second or even third consecutive measurement of sample pH.

For pH measurement in low-ionic strength solutions a stable pH reading can take 5 minutes or more to obtain, as the reading is affected by the exchange of carbon dioxide between the sample and the atmosphere, the effects of stirring and vibrations, and a mismatch between the ionic strength of the sample and the reference solution in the electrode. If after ~ 5 min the pH reading does not stabilize in a gently stirred sample, obtain a pH reading in the unstirred sample.

4. Sample management

Each participating laboratory will receive by mail one week ahead of the start date sufficient air-dried and sieved soil to test each material in duplicate for pH. The anticipated effort is ~1.5 person-hr. Treat each duplicate as an independent sample and run samples in a random order. Fill in Table 1 with the random order of sample analysis.

Table 1 Random Order of Sample Analysis

Sample	Sample Number	Order Analyzed
Material C, Replicate 1	1	
Material C, Replicate 2	2	
Material D, Replicate 1	3	
Material D, Replicate 2	4	

Visit the web site www.random.org (Figure 1). In the box labeled “True Random Number Generator” and enter 1 for Min and 4 for Max, then select the button for Generate. A result will appear. The first result to appear is the first sample to be analyzed; for example, if the first result is “1”, analyzed sample 1 first. Select the button for Generate again. If the second result is “4”, analyze sample 4 second, and so forth. Ignore a repeated result.

RANDOM.ORG

True Random Number Service

Do you own an iOS or Android device? Check out our app!

What's this fuss about *true* randomness?

Perhaps you have wondered how predictable machines like computers can generate randomness. In reality, most random numbers used in computer programs are *pseudo-random*, which means they are generated in a predictable fashion using a mathematical formula. This is fine for many purposes, but it may not be random in the way you expect if you're used to dice rolls and lottery drawings.

RANDOM.ORG offers *true* random numbers to anyone on the Internet. The randomness comes from atmospheric noise, which for many purposes is better than the pseudo-random number algorithms typically used in computer programs. People use RANDOM.ORG for holding drawings, lotteries and sweepstakes, to drive online games, for scientific applications and for art and music. The service has existed since 1998 and was built by Dr Mads Haahr of the School of Computer Science and Statistics at Trinity College, Dublin in Ireland. Today, RANDOM.ORG is operated by Randomness and Integrity Services Ltd.

As of today, RANDOM.ORG has generated 1.95 trillion random bits for the Internet community.

True Random Number Generator

Min: 1

Max: 4

Result:

1

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Keno Quick Pick for the popular game played in many countries
Coin Flipper will give you heads or tails in many currencies
Dice Roller does exactly what it says on the tin
Playing Card Shuffler will draw cards from multiple shuffled decks
Birdie Fund Generator will create birdie holes for golf courses

PAID service

Random Drawings

Q3.1 in the FAQ explains how to pick a winner for your giveaway for FREE
Third-Party Draw Service is the premier solution to holding random drawings online

Figure 1. Random number generator.

5. Data management

Data should be handled and reported as required by the revised FM. Upon completion of testing, submit the attached data sheet electronically to the study contact. Keep data records on file for at least one year past the study date.

References

1. ASTM C802-2009a Standard Practice for Conducting an Inter-Laboratory Test Program to Determine the Precision of Test Methods for Construction Materials. ASTM International, West Conshohocken, Pennsylvania. 18 pp.

2. ASTM C670-2003 Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials, ASTM International, West Conshohocken, Pennsylvania. 9 pp.

Data Sheet

Select Backfill (092L)

Complete and submit data sheet by e-mail to npoor@usf.edu on or before March 12, 2015.

Assigned Laboratory Number ________

Sample	pH, pH units	Sample Temperature, °C
Example	pH 7.01	25.0
Material C, Replicate 1		
Material C, Replicate 2		
Material D, Replicate 1		
Material D, Replicate 2		

Comments (type or print legibly):

Appendix D Analysis of Variance (ANOVA) for Replicate Study

D.1 ANOVA for pH

Table D-1 ANOVA for Replicate Study pH

ANOVA: Single Factor for pH

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Mine 1	12	55.92	4.66	0.0076
Mine 2	12	64.42	5.37	0.0486
Mine 3	12	97.85	8.15	0.0418
Mine 4	12	58.61	4.88	0.0384
Mine 5	12	55.74	4.65	0.0416
Mine 6	12	56.39	4.70	0.4013
Mine 7	12	88.80	7.40	0.0060
Mine 8	12	106.41	8.87	0.0006

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	261	7	37.3	509	2.66E-68	2.11
Within Groups	6.45	88	0.07			
Total	267.25	95				

D.2 ANOVA for Minimum Resistivity

Table D-2 Replicate Study ANOVA for Minimum Resistivity (ohm-cm)

ANOVA: Single Factor for Minimum Resistivity

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Mine 5	12	229,000	19,100	39,600,000
Mine 6	12	437,000	36,400	1.05E+08
Mine 7	12	400,000	33,300	13,000,000
Mine 8	12	151,000	12,500	23,400,000

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.66E+09	3	1.55E+09	38.0	1.87E-12	2.82
Within Groups	1.75E+09	44	39,900,000			
Total	6.42E+09	47				

D.3 ANOVA for Sulfate

Table D-3 Replicate Study ANOVA for Sulfate (ppm)

Anova: Single Factor for Sulfate

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Mine 1	12	153	13	39.5
Mine 3	12	405	34	917
Mine 5	12	288	24	16.4
Mine 6	12	117	10	14.9

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4,350	3	1,450	5.88	0.00183	2.82
Within Groups	10,900	44	247			
Total	15,200	47				

Appendix E PHREEQ Input and Output Files

E.1 Input File

```
SOLUTION 0 Rainwater #VW annual averages from NADP FL41 2000-2012
       units ppm
       pH           4.9 charge
       temp         25.0
       Ca           0.10
       Mg           0.04
       Na           0.3
       K            0.02
       Cl           0.68 #adjusted to keep pH at 4.9 in equilibrium with CO2
       S(+6)        0.7
SAVE SOLUTION 0
END

SOLUTION 1-60  Groundwater #from Shiffer, 1989
      units ppm
       pH          5
      temp          25.0
      Ca            0.4
       Mg           0.5
       Na           2.1
       K            0.1
       Cl           4.0
       S(+6)        0.6
       Alkalinity   0.82 as HCO3
SAVE SOLUTION 1 60
END

USE SOLUTION 0
EQUILIBRIUM_PHASES 0
       CO2(g)      -3.5
       QUARTZ  0.0
SAVE SOLUTION 0
END

USE SOLUTION 1 60
EQUILIBRIUM_PHASES 1-60
       CO2(g)      -1.9
       QUARTZ  0.0
SAVE SOLUTION 1 60
END

USE SOLUTION 0 60
EXCHANGE 1-60
       -equilibrate 1
      X                250 #from Elrashidi et al., 2001
COPY cell 1 60
ADVECTION
        -cells                   60
        -shifts            75 #15 shifts per year
         -time_step        0.06667 yr
         -initial_time           0
        -punch_cells       60
        -punch_frequency   1
         -print_cells            60
```

```
         -print_frequency      15
SELECTED_OUTPUT
        -file            exRainX.sel
        -reset           false
        -step
        -pH
        -totals          K Ca Na
USER_PUNCH
  -heading  Time
  10 PUNCH (STEP_NO)/15
END
```

E.2 Output File

```
(Partial printing of output file)

Input file: C:\Program Files (x86)\USGS\Phreeqc Interactive 3.0.6-
7757\examples\Rainwater and Groundwater Exchange 2.pqi
Output file: C:\Program Files (x86)\USGS\Phreeqc Interactive 3.0.6-
7757\examples\Rainwater and Groundwater Exchange 2.pqo
Database file: C:\Program Files (x86)\USGS\Phreeqc Interactive 3.0.6-
7757\database\phreeqc.dat

------------------
Reading data base.
------------------

       SOLUTION_MASTER_SPECIES
       SOLUTION_SPECIES
       PHASES
       EXCHANGE_MASTER_SPECIES
       EXCHANGE_SPECIES
       SURFACE_MASTER_SPECIES
       SURFACE_SPECIES
       RATES
       END
------------------------------------
Reading input data for simulation 1.
------------------------------------

       DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.0.6-
7757\database\phreeqc.dat
       TITLE Rainwater and Groundwater - Exchange
       SOLUTION 0 Rainwater #VW annual averages from NADP FL41 2000-2012
              units ppm
              pH           4.9 charge
              temp         25.0
              Ca           0.10
              Mg           0.04
              Na           0.3
              K            0.02
              Cl           0.68 #adjusted to keep pH at 4.9 in equilibrium with CO2
              S(+6)        0.7
       SAVE SOLUTION 0
       END
-----
TITLE
-----
```

```
 Rainwater and Groundwater - Exchange

-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 0. Rainwater

-----------------------------Solution composition------------------------------

       Elements           Molality       Moles

       Ca               2.495e-006  2.495e-006
       Cl               1.918e-005  1.918e-005
       K                5.115e-007  5.115e-007
       Mg               1.645e-006  1.645e-006
       Na               1.305e-005  1.305e-005
       S(6)             7.287e-006  7.287e-006

----------------------------Description of solution----------------------------

                                       pH  =   4.928      Charge balance
                                       pe  =   4.000
       Specific Conductance (uS/cm, 25 oC) = 7
                          Density (g/cm3)  =   0.99704
                               Volume (L)  =   1.00297
                        Activity of water  =   1.000
                           Ionic strength  =  4.514e-005
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  = -1.191e-005
                    Total carbon (mol/kg)  =  0.000e+000
                       Total CO2 (mol/kg)  =  0.000e+000
                      Temperature (deg C)  =  25.00
                  Electrical balance (eq)  =  8.272e-018
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =   3
                                  Total H  = 1.110124e+002
                                  Total O  = 5.550625e+001

----------------------------Distribution of species----------------------------

                                               Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol

   H+             1.191e-005  1.181e-005    -4.924    -4.928    -0.003      0.00
   OH-            8.635e-010  8.568e-010    -9.064    -9.067    -0.003     -4.13
   H2O            5.551e+001  1.000e+000     1.744    -0.000     0.000     18.07
Ca           2.495e-006
   Ca+2           2.492e-006  2.415e-006    -5.603    -5.617    -0.014    -18.23
   CaSO4          3.028e-009  3.028e-009    -8.519    -8.519     0.000      7.50
   CaHSO4+        2.370e-013  2.351e-013   -12.625   -12.629    -0.003     (0)
   CaOH+          3.420e-014  3.393e-014   -13.466   -13.469    -0.003     (0)
Cl           1.918e-005
   Cl-            1.918e-005  1.903e-005    -4.717    -4.721    -0.003     18.05
H(0)         1.976e-021
   H2             9.880e-022  9.880e-022   -21.005   -21.005     0.000     28.61
K            5.115e-007
   K+             5.115e-007  5.075e-007    -6.291    -6.295    -0.003      8.99
```

```
   KSO4-          2.533e-011  2.513e-011   -10.596   -10.600    -0.003     (0)
Mg           1.645e-006
   Mg+2           1.643e-006  1.592e-006    -5.784    -5.798    -0.014    -21.91
   MgSO4          2.631e-009  2.631e-009    -8.580    -8.580     0.000      5.84
   MgOH+          4.932e-013  4.894e-013   -12.307   -12.310    -0.003     (0)
Na           1.305e-005
   Na+            1.305e-005  1.295e-005    -4.884    -4.888    -0.003     -1.41
   NaSO4-         4.610e-010  4.574e-010    -9.336    -9.340    -0.003     18.39
   NaOH           1.109e-024  1.109e-024   -23.955   -23.955     0.000     (0)
O(0)         0.000e+000
   O2             0.000e+000  0.000e+000   -50.370   -50.370     0.000     30.40
S(6)         7.287e-006
   SO4-2          7.273e-006  7.049e-006    -5.138    -5.152    -0.014     13.92
   HSO4-          8.160e-009  8.096e-009    -8.088    -8.092    -0.003     40.25
   CaSO4          3.028e-009  3.028e-009    -8.519    -8.519     0.000      7.50
   MgSO4          2.631e-009  2.631e-009    -8.580    -8.580     0.000      5.84
   NaSO4-         4.610e-010  4.574e-010    -9.336    -9.340    -0.003     18.39
   KSO4-          2.533e-011  2.513e-011   -10.596   -10.600    -0.003     (0)
   CaHSO4+        2.370e-013  2.351e-013   -12.625   -12.629    -0.003     (0)

------------------------------Saturation indices-------------------------------

       Phase               SI   log IAP   log K(298 K,   1 atm)

       Anhydrite        -6.49    -10.77   -4.28  CaSO4
       Gypsum           -6.19    -10.77   -4.58  CaSO4:2H2O
       H2(g)           -17.90    -21.01   -3.10  H2
       H2O(g)           -1.50     -0.00    1.50  H2O
       Halite          -11.18     -9.61    1.57  NaCl
       O2(g)           -47.48    -50.37   -2.89  O2
       Sylvite         -11.91    -11.02    0.90  KCl


------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 2.
------------------------------------

       SOLUTION 1-60  Groundwater #from Shiffer, 1989
             units ppm
              pH          5
             temp          25.0
             Ca            0.4
              Mg           0.5
              Na           2.1
              K            0.1
              Cl           4.0
              S(+6)        0.6
              Alkalinity   0.82 as HCO3
       SAVE SOLUTION 1 60
       END
-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1. Groundwater
```

```
-----------------------------Solution composition------------------------------

      Elements           Molality       Moles

      Alkalinity       1.344e-005  1.344e-005
      Ca               9.980e-006  9.980e-006
      Cl               1.128e-004  1.128e-004
      K                2.557e-006  2.557e-006
      Mg               2.057e-005  2.057e-005
      Na               9.135e-005  9.135e-005
      S(6)             6.246e-006  6.246e-006

----------------------------Description of solution----------------------------

                                       pH  =   5.000
                                       pe  =   4.000
      Specific Conductance (uS/cm, 25 oC) = 22
                          Density (g/cm3)  =   0.99706
                               Volume (L)  =   1.00301
                        Activity of water  =   1.000
                           Ionic strength  =  1.937e-004
                       Mass of water (kg)  =  1.000e+000
                    Total carbon (mol/kg)  =  5.456e-004
                       Total CO2 (mol/kg)  =  5.456e-004
                      Temperature (deg C)  =  25.00
                  Electrical balance (eq)  =  1.624e-005
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   5.17
                               Iterations  =   6
                                  Total H  = 1.110125e+002
                                  Total O  = 5.550736e+001

----------------------------Distribution of species----------------------------

                                               Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol

   H+             1.016e-005  1.000e-005    -4.993    -5.000    -0.007      0.00
   OH-            1.029e-009  1.012e-009    -8.988    -8.995    -0.007     -4.13
   H2O            5.551e+001  1.000e+000     1.744    -0.000     0.000     18.07
C(4)         5.456e-004
   CO2            5.220e-004  5.220e-004    -3.282    -3.282     0.000     29.09
   HCO3-          2.359e-005  2.322e-005    -4.627    -4.634    -0.007     24.69
   MgHCO3+        5.319e-009  5.235e-009    -8.274    -8.281    -0.007      5.46
   CaHCO3+        2.815e-009  2.770e-009    -8.551    -8.557    -0.007      9.66
   NaHCO3         1.174e-009  1.174e-009    -8.930    -8.930     0.000      2.13
   CO3-2          1.161e-010  1.089e-010    -9.935    -9.963    -0.028     -5.58
   MgCO3          2.002e-012  2.002e-012   -11.699   -11.699     0.000    -17.09
   CaCO3          1.710e-012  1.711e-012   -11.767   -11.767     0.000    -14.60
   NaCO3-         1.852e-013  1.823e-013   -12.732   -12.739    -0.007     -0.63
Ca           9.980e-006
   Ca+2           9.968e-006  9.351e-006    -5.001    -5.029    -0.028    -18.20
   CaSO4          9.673e-009  9.674e-009    -8.014    -8.014     0.000      7.50
   CaHCO3+        2.815e-009  2.770e-009    -8.551    -8.557    -0.007      9.66
   CaCO3          1.710e-012  1.711e-012   -11.767   -11.767     0.000    -14.60
   CaHSO4+        6.462e-013  6.359e-013   -12.190   -12.197    -0.007     (0)
   CaOH+          1.577e-013  1.552e-013   -12.802   -12.809    -0.007     (0)
Cl           1.128e-004
   Cl-            1.128e-004  1.110e-004    -3.948    -3.955    -0.007     18.06
```

```
H(0)         1.416e-021
   H2              7.079e-022  7.079e-022   -21.150   -21.150     0.000     28.61
K            2.557e-006
   K+              2.557e-006  2.517e-006    -5.592    -5.599    -0.007      8.99
   KSO4-           1.045e-010  1.029e-010    -9.981    -9.988    -0.007     (0)
Mg           2.057e-005
   Mg+2            2.053e-005  1.927e-005    -4.688    -4.715    -0.028    -21.89
   MgSO4           2.627e-008  2.628e-008    -7.580    -7.580     0.000      5.84
   MgHCO3+         5.319e-009  5.235e-009    -8.274    -8.281    -0.007      5.46
   MgOH+           7.108e-012  6.996e-012   -11.148   -11.155    -0.007     (0)
   MgCO3           2.002e-012  2.002e-012   -11.699   -11.699     0.000    -17.09
Na           9.135e-005
   Na+             9.134e-005  8.989e-005    -4.039    -4.046    -0.007     -1.41
   NaSO4-          2.663e-009  2.621e-009    -8.575    -8.582    -0.007     18.40
   NaHCO3          1.174e-009  1.174e-009    -8.930    -8.930     0.000      2.13
   NaCO3-          1.852e-013  1.823e-013   -12.732   -12.739    -0.007     -0.63
   NaOH            9.098e-024  9.098e-024   -23.041   -23.041     0.000     (0)
O(0)         0.000e+000
   O2              0.000e+000  0.000e+000   -50.080   -50.080     0.000     30.40
S(6)         6.246e-006
   SO4-2           6.201e-006  5.817e-006    -5.208    -5.235    -0.028     13.95
   MgSO4           2.627e-008  2.628e-008    -7.580    -7.580     0.000      5.84
   CaSO4           9.673e-009  9.674e-009    -8.014    -8.014     0.000      7.50
   HSO4-           5.747e-009  5.656e-009    -8.241    -8.247    -0.007     40.26
   NaSO4-          2.663e-009  2.621e-009    -8.575    -8.582    -0.007     18.40
   KSO4-           1.045e-010  1.029e-010    -9.981    -9.988    -0.007     (0)
   CaHSO4+         6.462e-013  6.359e-013   -12.190   -12.197    -0.007     (0)

------------------------------Saturation indices-------------------------------

       Phase               SI   log IAP   log K(298 K,   1 atm)

       Anhydrite        -5.99    -10.26   -4.28  CaSO4
       Aragonite        -6.66    -14.99   -8.34  CaCO3
       Calcite          -6.51    -14.99   -8.48  CaCO3
       CO2(g)           -1.82     -3.28   -1.46  CO2
       Dolomite        -12.58    -29.67  -17.09  CaMg(CO3)2
       Gypsum           -5.68    -10.26   -4.58  CaSO4:2H2O
       H2(g)           -18.05    -21.15   -3.10  H2
       H2O(g)           -1.50     -0.00    1.50  H2O
       Halite           -9.57     -8.00    1.57  NaCl
       O2(g)           -47.19    -50.08   -2.89  O2
       Sylvite         -10.45     -9.55    0.90  KCl


------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 3.
------------------------------------

       USE SOLUTION 0
       EQUILIBRIUM_PHASES 0
              CO2(g)      -3.5
              QUARTZ  0.0
       SAVE SOLUTION 0
       END
```

```
-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 0.   Rainwater
Using pure phase assemblage 0.

-------------------------------Phase assemblage--------------------------------

                                                      Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)           -3.50    -4.96     -1.46   1.000e+001  1.000e+001 -1.133e-005
Quartz           -0.00    -3.98     -3.98   1.000e+001  1.000e+001 -1.046e-004

-----------------------------Solution composition------------------------------

      Elements           Molality       Moles

      C                1.133e-005  1.133e-005
      Ca               2.495e-006  2.495e-006
      Cl               1.918e-005  1.918e-005
      K                5.115e-007  5.115e-007
      Mg               1.645e-006  1.645e-006
      Na               1.305e-005  1.305e-005
      S                7.287e-006  7.287e-006
      Si               1.046e-004  1.046e-004

----------------------------Description of solution----------------------------

                                       pH  =   4.913      Charge balance
                                       pe  =   0.438      Adjusted to redox
equilibrium
       Specific Conductance (uS/cm, 25 oC) = 8
                          Density (g/cm3)  =   0.99705
                               Volume (L)  =   1.00297
                        Activity of water  =   1.000
                           Ionic strength  =  4.554e-005
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  = -1.191e-005
                       Total CO2 (mol/kg)  =  1.133e-005
                      Temperature (deg C)  =  25.00
                  Electrical balance (eq)  =  8.277e-018
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                               Iterations  =  11
                                  Total H  = 1.110124e+002
                                  Total O  = 5.550648e+001

----------------------------Distribution of species----------------------------

                                               Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol

   H+             1.231e-005  1.221e-005    -4.910    -4.913    -0.003      0.00
   OH-            8.353e-010  8.288e-010    -9.078    -9.082    -0.003     -4.13
   H2O            5.551e+001  1.000e+000     1.744    -0.000     0.000     18.07
C(-4)        4.144e-024
```

```
   CH4            4.144e-024  4.144e-024   -23.383   -23.383     0.000     32.22
C(4)          1.133e-005
   CO2            1.093e-005  1.093e-005    -4.961    -4.961     0.000     29.09
   HCO3-          4.012e-007  3.981e-007    -6.397    -6.400    -0.003     24.69
   CaHCO3+        1.236e-011  1.227e-011   -10.908   -10.911    -0.003      9.65
   MgHCO3+        7.474e-012  7.415e-012   -11.126   -11.130    -0.003      5.45
   NaHCO3         2.898e-012  2.898e-012   -11.538   -11.538     0.000      2.13
   CO3-2          1.577e-012  1.529e-012   -11.802   -11.816    -0.014     -5.60
   CaCO3          6.202e-015  6.202e-015   -14.207   -14.207     0.000    -14.60
   MgCO3          2.322e-015  2.322e-015   -14.634   -14.634     0.000    -17.09
   NaCO3-         3.714e-016  3.685e-016   -15.430   -15.434    -0.003     -0.64
Ca            2.495e-006
   Ca+2           2.492e-006  2.415e-006    -5.603    -5.617    -0.014    -18.23
   CaSO4          3.027e-009  3.027e-009    -8.519    -8.519     0.000      7.50
   CaHCO3+        1.236e-011  1.227e-011   -10.908   -10.911    -0.003      9.65
   CaHSO4+        2.449e-013  2.430e-013   -12.611   -12.614    -0.003     (0)
   CaOH+          3.308e-014  3.282e-014   -13.480   -13.484    -0.003     (0)
   CaCO3          6.202e-015  6.202e-015   -14.207   -14.207     0.000    -14.60
Cl            1.918e-005
   Cl-            1.918e-005  1.903e-005    -4.717    -4.721    -0.003     18.05
H(0)          2.806e-014
   H2             1.403e-014  1.403e-014   -13.853   -13.853     0.000     28.61
K             5.115e-007
   K+             5.115e-007  5.075e-007    -6.291    -6.295    -0.003      8.99
   KSO4-          2.533e-011  2.513e-011   -10.596   -10.600    -0.003     (0)
Mg            1.645e-006
   Mg+2           1.643e-006  1.592e-006    -5.784    -5.798    -0.014    -21.91
   MgSO4          2.630e-009  2.630e-009    -8.580    -8.580     0.000      5.84
   MgHCO3+        7.474e-012  7.415e-012   -11.126   -11.130    -0.003      5.45
   MgOH+          4.770e-013  4.733e-013   -12.321   -12.325    -0.003     (0)
   MgCO3          2.322e-015  2.322e-015   -14.634   -14.634     0.000    -17.09
Na            1.305e-005
   Na+            1.305e-005  1.295e-005    -4.884    -4.888    -0.003     -1.41
   NaSO4-         4.609e-010  4.573e-010    -9.336    -9.340    -0.003     18.39
   NaHCO3         2.898e-012  2.898e-012   -11.538   -11.538     0.000      2.13
   NaCO3-         3.714e-016  3.685e-016   -15.430   -15.434    -0.003     -0.64
   NaOH           1.073e-024  1.073e-024   -23.969   -23.969     0.000     (0)
O(0)          0.000e+000
   O2             0.000e+000  0.000e+000   -64.674   -64.674     0.000     30.40
S(-2)         6.396e-018
   H2S            6.337e-018  6.337e-018   -17.198   -17.198     0.000     37.16
   HS-            5.981e-020  5.934e-020   -19.223   -19.227    -0.003     20.58
   S-2            6.056e-028  5.869e-028   -27.218   -27.231    -0.014     (0)
S(6)          7.287e-006
   SO4-2          7.272e-006  7.048e-006    -5.138    -5.152    -0.014     13.92
   HSO4-          8.434e-009  8.368e-009    -8.074    -8.077    -0.003     40.25
   CaSO4          3.027e-009  3.027e-009    -8.519    -8.519     0.000      7.50
   MgSO4          2.630e-009  2.630e-009    -8.580    -8.580     0.000      5.84
   NaSO4-         4.609e-010  4.573e-010    -9.336    -9.340    -0.003     18.39
   KSO4-          2.533e-011  2.513e-011   -10.596   -10.600    -0.003     (0)
   CaHSO4+        2.449e-013  2.430e-013   -12.611   -12.614    -0.003     (0)
Si            1.046e-004
   H4SiO4         1.046e-004  1.046e-004    -3.980    -3.980     0.000     52.08
   H3SiO4-        1.273e-009  1.263e-009    -8.895    -8.899    -0.003     27.95
   H2SiO4-2       7.259e-018  7.035e-018   -17.139   -17.153    -0.014     (0)

------------------------------Saturation indices-------------------------------

       Phase               SI   log IAP   log K(298 K,   1 atm)
```

```
      Anhydrite        -6.49    -10.77   -4.28  CaSO4
      Aragonite        -9.10    -17.43   -8.34  CaCO3
      Calcite          -8.95    -17.43   -8.48  CaCO3
      CH4(g)          -20.54    -23.38   -2.84  CH4
      Chalcedony       -0.43     -3.98   -3.55  SiO2
      Chrysotile      -28.08      4.12   32.20  Mg3Si2O5(OH)4
      CO2(g)           -3.50     -4.96   -1.46  CO2   Pressure   0.0 atm, phi 1.000
      Dolomite        -17.96    -35.05  -17.09  CaMg(CO3)2
      Gypsum           -6.19    -10.77   -4.58  CaSO4:2H2O
      H2(g)           -10.75    -13.85   -3.10  H2
      H2O(g)           -1.50     -0.00    1.50  H2O
      H2S(g)          -16.15    -24.14   -7.99  H2S
      Halite          -11.18     -9.61    1.57  NaCl
      O2(g)           -61.78    -64.67   -2.89  O2
      Quartz           -0.00     -3.98   -3.98  SiO2
      Sepiolite       -19.64     -3.88   15.76  Mg2Si3O7.5OH:3H2O
      Sepiolite(d)    -22.54     -3.88   18.66  Mg2Si3O7.5OH:3H2O
      SiO2(a)          -1.27     -3.98   -2.71  SiO2
      Sulfur          -11.38     -6.50    4.88  S
      Sylvite         -11.91    -11.02    0.90  KCl
      Talc            -25.24     -3.84   21.40  Mg3Si4O10(OH)2


------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 4.
------------------------------------

      USE SOLUTION 1 60
      EQUILIBRIUM_PHASES 1-60
            CO2(g)      -1.9
            QUARTZ  0.0
      SAVE SOLUTION 1 60
      END
-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 1.   Groundwater
Using pure phase assemblage 1.

-------------------------------Phase assemblage--------------------------------

                                                      Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)           -1.90    -3.36     -1.46   1.000e+001  1.000e+001  8.817e-005
Quartz            0.00    -3.98     -3.98   1.000e+001  1.000e+001 -1.046e-004

-----------------------------Solution composition------------------------------

      Elements           Molality       Moles
```

```
       C                4.575e-004  4.575e-004
       Ca               9.980e-006  9.980e-006
       Cl               1.128e-004  1.128e-004
       K                2.557e-006  2.557e-006
       Mg               2.057e-005  2.057e-005
       Na               9.135e-005  9.135e-005
       S                6.246e-006  6.246e-006
       Si               1.046e-004  1.046e-004

----------------------------Description of solution-----------------------------

                                       pH  =   5.056      Charge balance
                                       pe  =   0.487      Adjusted to redox
equilibrium
       Specific Conductance (uS/cm, 25 oC) = 21
                          Density (g/cm3)  =   0.99706
                               Volume (L)  =   1.00301
                        Activity of water  =   1.000
                           Ionic strength  =  1.924e-004
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.344e-005
                       Total CO2 (mol/kg)  =  4.575e-004
                      Temperature (deg C)  =  25.00
                  Electrical balance (eq)  =  1.624e-005
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   5.21
                               Iterations  =  11
                                  Total H  = 1.110125e+002
                                  Total O  = 5.550739e+001

----------------------------Distribution of species----------------------------

                                               Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol

   H+             8.931e-006  8.792e-006    -5.049    -5.056    -0.007      0.00
   OH-            1.170e-009  1.151e-009    -8.932    -8.939    -0.007     -4.13
   H2O            5.551e+001  1.000e+000     1.744    -0.000     0.000     18.07
C(-4)        4.815e-024
   CH4            4.815e-024  4.815e-024   -23.317   -23.317     0.000     32.22
C(4)         4.575e-004
   CO2            4.351e-004  4.351e-004    -3.361    -3.361     0.000     29.09
   HCO3-          2.236e-005  2.201e-005    -4.650    -4.657    -0.007     24.69
   MgHCO3+        5.043e-009  4.963e-009    -8.297    -8.304    -0.007      5.46
   CaHCO3+        2.668e-009  2.626e-009    -8.574    -8.581    -0.007      9.66
   NaHCO3         1.113e-009  1.113e-009    -8.954    -8.954     0.000      2.13
   CO3-2          1.251e-010  1.174e-010    -9.903    -9.930    -0.028     -5.58
   MgCO3          2.159e-012  2.159e-012   -11.666   -11.666     0.000    -17.09
   CaCO3          1.845e-012  1.845e-012   -11.734   -11.734     0.000    -14.60
   NaCO3-         1.997e-013  1.965e-013   -12.700   -12.707    -0.007     -0.63
Ca           9.980e-006
   Ca+2           9.968e-006  9.353e-006    -5.001    -5.029    -0.028    -18.20
   CaSO4          9.678e-009  9.679e-009    -8.014    -8.014     0.000      7.50
   CaHCO3+        2.668e-009  2.626e-009    -8.574    -8.581    -0.007      9.66
   CaCO3          1.845e-012  1.845e-012   -11.734   -11.734     0.000    -14.60
   CaHSO4+        5.684e-013  5.594e-013   -12.245   -12.252    -0.007     (0)
   CaOH+          1.794e-013  1.765e-013   -12.746   -12.753    -0.007     (0)
Cl           1.128e-004
   Cl-            1.128e-004  1.110e-004    -3.948    -3.955    -0.007     18.06
H(0)         1.160e-014
```

```
   H2             5.800e-015  5.800e-015   -14.237   -14.237     0.000     28.61
K             2.557e-006
   K+             2.557e-006  2.517e-006    -5.592    -5.599    -0.007      8.99
   KSO4-          1.046e-010  1.029e-010    -9.981    -9.988    -0.007     (0)
Mg            2.057e-005
   Mg+2           2.053e-005  1.927e-005    -4.688    -4.715    -0.028    -21.89
   MgSO4          2.629e-008  2.629e-008    -7.580    -7.580     0.000      5.84
   MgHCO3+        5.043e-009  4.963e-009    -8.297    -8.304    -0.007      5.46
   MgOH+          8.085e-012  7.958e-012   -11.092   -11.099    -0.007     (0)
   MgCO3          2.159e-012  2.159e-012   -11.666   -11.666     0.000    -17.09
Na            9.135e-005
   Na+            9.134e-005  8.990e-005    -4.039    -4.046    -0.007     -1.41
   NaSO4-         2.664e-009  2.622e-009    -8.574    -8.581    -0.007     18.40
   NaHCO3         1.113e-009  1.113e-009    -8.954    -8.954     0.000      2.13
   NaCO3-         1.997e-013  1.965e-013   -12.700   -12.707    -0.007     -0.63
   NaOH           1.035e-023  1.035e-023   -22.985   -22.985     0.000     (0)
O(0)          0.000e+000
   O2             0.000e+000  0.000e+000   -63.907   -63.907     0.000     30.40
S(-2)         8.020e-020
   H2S            7.916e-020  7.916e-020   -19.102   -19.101     0.000     37.16
   HS-            1.046e-021  1.030e-021   -20.980   -20.987    -0.007     20.59
   S-2            1.508e-029  1.415e-029   -28.822   -28.849    -0.028     (0)
S(6)          6.246e-006
   SO4-2          6.202e-006  5.819e-006    -5.207    -5.235    -0.028     13.95
   MgSO4          2.629e-008  2.629e-008    -7.580    -7.580     0.000      5.84
   CaSO4          9.678e-009  9.679e-009    -8.014    -8.014     0.000      7.50
   HSO4-          5.055e-009  4.974e-009    -8.296    -8.303    -0.007     40.26
   NaSO4-         2.664e-009  2.622e-009    -8.574    -8.581    -0.007     18.40
   KSO4-          1.046e-010  1.029e-010    -9.981    -9.988    -0.007     (0)
   CaHSO4+        5.684e-013  5.594e-013   -12.245   -12.252    -0.007     (0)
Si            1.046e-004
   H4SiO4         1.046e-004  1.046e-004    -3.980    -3.980     0.000     52.08
   H3SiO4-        1.783e-009  1.754e-009    -8.749    -8.756    -0.007     27.96
   H2SiO4-2       1.446e-017  1.357e-017   -16.840   -16.867    -0.028     (0)

------------------------------Saturation indices-------------------------------

       Phase               SI   log IAP   log K(298 K,   1 atm)

       Anhydrite        -5.99    -10.26   -4.28  CaSO4
       Aragonite        -6.62    -14.96   -8.34  CaCO3
       Calcite          -6.48    -14.96   -8.48  CaCO3
       CH4(g)          -20.47    -23.32   -2.84  CH4
       Chalcedony       -0.43     -3.98   -3.55  SiO2
       Chrysotile      -23.97      8.23   32.20  Mg3Si2O5(OH)4
       CO2(g)           -1.90     -3.36   -1.46  CO2   Pressure   0.0 atm, phi 1.000
       Dolomite        -12.51    -29.60  -17.09  CaMg(CO3)2
       Gypsum           -5.68    -10.26   -4.58  CaSO4:2H2O
       H2(g)           -11.14    -14.24   -3.10  H2
       H2O(g)           -1.50     -0.00    1.50  H2O
       H2S(g)          -18.05    -26.04   -7.99  H2S
       Halite           -9.57     -8.00    1.57  NaCl
       O2(g)           -61.01    -63.91   -2.89  O2
       Quartz            0.00     -3.98   -3.98  SiO2
       Sepiolite       -16.91     -1.15   15.76  Mg2Si3O7.5OH:3H2O
       Sepiolite(d)    -19.81     -1.15   18.66  Mg2Si3O7.5OH:3H2O
       SiO2(a)          -1.27     -3.98   -2.71  SiO2
       Sulfur          -12.90     -8.01    4.88  S
       Sylvite         -10.45     -9.55    0.90  KCl
```

```
      Talc            -21.13      0.27   21.40  Mg3Si4O10(OH)2


------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 5.
------------------------------------

      USE SOLUTION 0 60
      EXCHANGE 1-60
             equilibrate 1
            X               250 #from Elrashidi et al., 2001
      COPY cell 1 60
      ADVECTION
              cells                    60
              shifts             75 #15 shifts per year
               time_step         0.06667 yr
               initial_time            0
              punch_cells        60
              punch_frequency    1
               print_cells       60
               print_frequency      15
      SELECTED_OUTPUT
              file            exRainX.sel
              reset           false
              step
              ph
              totals          K Ca Na
      USER_PUNCH
        heading  Time
        10 PUNCH (STEP_NO)/15
      END
-------------------------------------------------------
Beginning of initial exchange-composition calculations.
-------------------------------------------------------

Exchange 1.

X              2.500e+002 mol

                                   Equiv-    Equivalent      Log
      Species             Moles      alents      Fraction     Gamma

      MgX2           7.004e+001  1.401e+002  5.603e-001    -0.028
      CaX2           5.388e+001  1.078e+002  4.311e-001    -0.028
      NaX            1.891e+000  1.891e+000  7.562e-003    -0.007
      KX             2.653e-001  2.653e-001  1.061e-003    -0.007

-----------------------------------------
Beginning of batch-reaction calculations.
-----------------------------------------

Reaction step 1.

Using solution 0.   Solution after simulation 3.
Using exchange 1.   Exchange assemblage after simulation 5.
```

```
-----------------------------Exchange composition------------------------------

X               2.500e+002 mol

                                      Equiv-    Equivalent      Log 
       Species             Moles      alents      Fraction     Gamma

       MgX2             7.004e+001  1.401e+002  5.603e-001    -0.013
       CaX2             5.388e+001  1.078e+002  4.311e-001    -0.013
       NaX              1.891e+000  1.891e+000  7.562e-003    -0.003
       KX               2.653e-001  2.653e-001  1.061e-003    -0.003

-----------------------------Solution composition------------------------------

       Elements           Molality       Moles

       C                1.133e-005  1.133e-005
       Ca               4.202e-007  4.202e-007
       Cl               1.918e-005  1.918e-005
       K                5.248e-007  5.248e-007
       Mg               8.661e-007  8.661e-007
       Na               1.874e-005  1.874e-005
       S                7.287e-006  7.287e-006
       Si               1.046e-004  1.046e-004

----------------------------Description of solution----------------------------

                                       pH  =   4.913      Charge balance
                                       pe  =   0.197      Adjusted to redox 
equilibrium
       Specific Conductance (uS/cm, 25 oC) = 8
                          Density (g/cm3)  =   0.99705
                               Volume (L)  =   1.00297
                        Activity of water  =   1.000
                           Ionic strength  =  4.270e-005
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  = -1.191e-005
                       Total CO2 (mol/kg)  =  1.133e-005
                      Temperature (deg C)  =  25.00
                  Electrical balance (eq)  = -1.306e-017
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                               Iterations  =  71
                                  Total H  = 1.110124e+002
                                  Total O  = 5.550648e+001

----------------------------Distribution of species----------------------------

                                               Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol

   H+             1.231e-005  1.222e-005    -4.910    -4.913    -0.003      0.00
   OH-            8.349e-010  8.286e-010    -9.078    -9.082    -0.003     -4.13
   H2O            5.551e+001  1.000e+000     1.744    -0.000     0.000     18.07
C(-4)        3.549e-022
   CH4            3.549e-022  3.549e-022   -21.450   -21.450     0.000     32.22
C(4)         1.133e-005
   CO2            1.093e-005  1.093e-005    -4.961    -4.961     0.000     29.09
   HCO3-          4.010e-007  3.980e-007    -6.397    -6.400    -0.003     24.69
```

```
   NaHCO3         4.163e-012  4.163e-012    -11.381    -11.381    0.000      2.13
   MgHCO3+        3.936e-012  3.906e-012    -11.405    -11.408   -0.003      5.45
   CaHCO3+        2.083e-012  2.067e-012    -11.681    -11.685   -0.003      9.65
   CO3-2          1.575e-012  1.528e-012    -11.803    -11.816   -0.013     -5.60
   MgCO3          1.223e-015  1.223e-015    -14.913    -14.913    0.000    -17.09
   CaCO3          1.045e-015  1.045e-015    -14.981    -14.981    0.000    -14.60
   NaCO3-         5.333e-016  5.293e-016    -15.273    -15.276   -0.003     -0.64
Ca           4.202e-007
   Ca+2           4.197e-007  4.072e-007     -6.377     -6.390   -0.013    -18.23
   CaSO4          5.110e-010  5.110e-010     -9.292     -9.292    0.000      7.50
   CaHCO3+        2.083e-012  2.067e-012    -11.681    -11.685   -0.003      9.65
   CaHSO4+        4.135e-014  4.103e-014    -13.384    -13.387   -0.003     (0)
   CaOH+          5.574e-015  5.532e-015    -14.254    -14.257   -0.003     (0)
   CaCO3          1.045e-015  1.045e-015    -14.981    -14.981    0.000    -14.60
Cl           1.918e-005
   Cl-            1.918e-005  1.903e-005     -4.717     -4.720   -0.003     18.05
H(0)         8.538e-014
   H2             4.269e-014  4.269e-014    -13.370    -13.370    0.000     28.61
K            5.248e-007
   K+             5.248e-007  5.208e-007     -6.280     -6.283   -0.003      8.99
   KSO4-          2.602e-011  2.583e-011    -10.585    -10.588   -0.003     (0)
Mg           8.661e-007
   Mg+2           8.647e-007  8.388e-007     -6.063     -6.076   -0.013    -21.91
   MgSO4          1.388e-009  1.388e-009     -8.858     -8.858    0.000      5.84
   MgHCO3+        3.936e-012  3.906e-012    -11.405    -11.408   -0.003      5.45
   MgOH+          2.512e-013  2.493e-013    -12.600    -12.603   -0.003     (0)
   MgCO3          1.223e-015  1.223e-015    -14.913    -14.913    0.000    -17.09
Na           1.874e-005
   Na+            1.874e-005  1.860e-005     -4.727     -4.730   -0.003     -1.41
   NaSO4-         6.630e-010  6.580e-010     -9.178     -9.182   -0.003     18.39
   NaHCO3         4.163e-012  4.163e-012    -11.381    -11.381    0.000      2.13
   NaCO3-         5.333e-016  5.293e-016    -15.273    -15.276   -0.003     -0.64
   NaOH           1.541e-024  1.541e-024    -23.812    -23.812    0.000     (0)
O(0)         0.000e+000
   O2             0.000e+000  0.000e+000    -65.641    -65.641    0.000     30.40
S(-2)        5.489e-016
   H2S            5.438e-016  5.438e-016    -15.265    -15.265    0.000     37.16
   HS-            5.130e-018  5.091e-018    -17.290    -17.293   -0.003     20.58
   S-2            5.190e-026  5.034e-026    -25.285    -25.298   -0.013     (0)
S(6)         7.287e-006
   SO4-2          7.276e-006  7.058e-006     -5.138     -5.151   -0.013     13.92
   HSO4-          8.446e-009  8.382e-009     -8.073     -8.077   -0.003     40.25
   MgSO4          1.388e-009  1.388e-009     -8.858     -8.858    0.000      5.84
   NaSO4-         6.630e-010  6.580e-010     -9.178     -9.182   -0.003     18.39
   CaSO4          5.110e-010  5.110e-010     -9.292     -9.292    0.000      7.50
   KSO4-          2.602e-011  2.583e-011    -10.585    -10.588   -0.003     (0)
   CaHSO4+        4.135e-014  4.103e-014    -13.384    -13.387   -0.003     (0)
Si           1.046e-004
   H4SiO4         1.046e-004  1.046e-004     -3.980     -3.980    0.000     52.08
   H3SiO4-        1.272e-009  1.263e-009     -8.895     -8.899   -0.003     27.95
   H2SiO4-2       7.249e-018  7.032e-018    -17.140    -17.153   -0.013     (0)

------------------------------Saturation indices-------------------------------

       Phase               SI   log IAP   log K(298 K,   1 atm)

       Anhydrite        -7.26    -11.54   -4.28  CaSO4
       Aragonite        -9.87    -18.21   -8.34  CaCO3
       Calcite          -9.73    -18.21   -8.48  CaCO3
```

```
       CH4(g)          -18.61    -21.45   -2.84  CH4
       Chalcedony       -0.43     -3.98   -3.55  SiO2
       Chrysotile      -28.91      3.29   32.20  Mg3Si2O5(OH)4
       CO2(g)           -3.50     -4.96   -1.46  CO2
       Dolomite        -19.01    -36.10  -17.09  CaMg(CO3)2
       Gypsum           -6.96    -11.54   -4.58  CaSO4:2H2O
       H2(g)           -10.27    -13.37   -3.10  H2
       H2O(g)           -1.50     -0.00    1.50  H2O
       H2S(g)          -14.21    -22.21   -7.99  H2S
       Halite          -11.02     -9.45    1.57  NaCl
       O2(g)           -62.75    -65.64   -2.89  O2
       Quartz           -0.00     -3.98   -3.98  SiO2
       Sepiolite       -20.20     -4.44   15.76  Mg2Si3O7.5OH:3H2O
       Sepiolite(d)    -23.10     -4.44   18.66  Mg2Si3O7.5OH:3H2O
       SiO2(a)          -1.27     -3.98   -2.71  SiO2
       Sulfur           -9.93     -5.04    4.88  S
       Sylvite         -11.90    -11.00    0.90  KCl
       Talc            -26.07     -4.67   21.40  Mg3Si4O10(OH)2


------------------------------------
Beginning of advection calculations.
------------------------------------

Beginning of advection time step 1, cumulative pore volumes 0.016667.
Beginning of advection time step 2, cumulative pore volumes 0.033333.
Beginning of advection time step 3, cumulative pore volumes 0.050000.
Beginning of advection time step 4, cumulative pore volumes 0.066667.
Beginning of advection time step 5, cumulative pore volumes 0.083333.
Beginning of advection time step 6, cumulative pore volumes 0.100000.
Beginning of advection time step 7, cumulative pore volumes 0.116667.
Beginning of advection time step 8, cumulative pore volumes 0.133333.
Beginning of advection time step 9, cumulative pore volumes 0.150000.
Beginning of advection time step 10, cumulative pore volumes 0.166667.
Beginning of advection time step 11, cumulative pore volumes 0.183333.
Beginning of advection time step 12, cumulative pore volumes 0.200000.
Beginning of advection time step 13, cumulative pore volumes 0.216667.
Beginning of advection time step 14, cumulative pore volumes 0.233333.
Beginning of advection time step 15, cumulative pore volumes 0.250000.

Cell 60.

Using solution 60.  Solution after simulation 5.
Using exchange 60.  Exchange assemblage after simulation 5.
Using pure phase assemblage 60.  Pure-phase assemblage after simulation 5.

-------------------------------Phase assemblage--------------------------------

                                                      Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)           -1.90    -3.36     -1.46   1.000e+001  1.000e+001  0.000e+000
Quartz            0.00    -3.98     -3.98   1.000e+001  1.000e+001  0.000e+000

-----------------------------Exchange composition------------------------------

X               2.500e+002 mol

                                      Equiv-    Equivalent      Log
```

```
       Species               Moles      alents    Fraction     Gamma

       MgX2             7.004e+001  1.401e+002  5.603e-001    -0.028
       CaX2             5.388e+001  1.078e+002  4.311e-001    -0.028
       NaX              1.891e+000  1.891e+000  7.562e-003    -0.007
       KX               2.653e-001  2.653e-001  1.061e-003    -0.007

------------------------------Solution composition------------------------------

       Elements           Molality       Moles

       C                4.575e-004  4.575e-004
       Ca               9.980e-006  9.980e-006
       Cl               1.128e-004  1.128e-004
       K                2.557e-006  2.557e-006
       Mg               2.057e-005  2.057e-005
       Na               9.135e-005  9.135e-005
       S                6.246e-006  6.246e-006
       Si               1.046e-004  1.046e-004

-----------------------------Description of solution----------------------------

                                        pH  =   5.056      Charge balance
                                        pe  =  -0.213      Adjusted to redox
equilibrium
       Specific Conductance (uS/cm, 25 oC) = 21
                           Density (g/cm3)  =   0.99706
                                Volume (L)  =   1.00301
                         Activity of water  =   1.000
                            Ionic strength  =  1.924e-004
                        Mass of water (kg)  =  1.000e+000
                  Total alkalinity (eq/kg)  =  1.344e-005
                        Total CO2 (mol/kg)  =  4.575e-004
                       Temperature (deg C)  =  25.00
                   Electrical balance (eq)  =  1.624e-005
  Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   5.21
                                Iterations  =   1
                                   Total H  = 1.110125e+002
                                   Total O  = 5.550739e+001

-----------------------------Distribution of species----------------------------

                                                Log       Log       Log    mole V
   Species           Molality    Activity  Molality  Activity     Gamma   cm3/mol

   H+              8.931e-006  8.792e-006    -5.049    -5.056    -0.007      0.00
   OH-             1.170e-009  1.151e-009    -8.932    -8.939    -0.007     -4.13
   H2O             5.551e+001  1.000e+000     1.744    -0.000     0.000     18.07
C(-4)        1.923e-018
   CH4             1.923e-018  1.923e-018   -17.716   -17.716     0.000     32.22
C(4)         4.575e-004
   CO2             4.351e-004  4.351e-004    -3.361    -3.361     0.000     29.09
   HCO3-           2.236e-005  2.201e-005    -4.650    -4.657    -0.007     24.69
   MgHCO3+         5.043e-009  4.963e-009    -8.297    -8.304    -0.007      5.46
   CaHCO3+         2.668e-009  2.626e-009    -8.574    -8.581    -0.007      9.66
   NaHCO3          1.113e-009  1.113e-009    -8.954    -8.954     0.000      2.13
   CO3-2           1.251e-010  1.174e-010    -9.903    -9.930    -0.028     -5.58
   MgCO3           2.159e-012  2.159e-012   -11.666   -11.666     0.000    -17.09
   CaCO3           1.845e-012  1.845e-012   -11.734   -11.734     0.000    -14.60
```

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   NaCO3-         1.997e-013  1.965e-013   -12.700   -12.707    -0.007     -0.63
Ca            9.980e-006
   Ca+2           9.968e-006  9.353e-006    -5.001    -5.029    -0.028    -18.20
   CaSO4          9.678e-009  9.679e-009    -8.014    -8.014     0.000      7.50
   CaHCO3+        2.668e-009  2.626e-009    -8.574    -8.581    -0.007      9.66
   CaCO3          1.845e-012  1.845e-012   -11.734   -11.734     0.000    -14.60
   CaHSO4+        5.684e-013  5.594e-013   -12.245   -12.252    -0.007     (0)
   CaOH+          1.794e-013  1.765e-013   -12.746   -12.753    -0.007     (0)
Cl            1.128e-004
   Cl-            1.128e-004  1.110e-004    -3.948    -3.955    -0.007     18.06
H(0)          2.916e-013
   H2             1.458e-013  1.458e-013   -12.836   -12.836     0.000     28.61
K             2.557e-006
   K+             2.557e-006  2.517e-006    -5.592    -5.599    -0.007      8.99
   KSO4-          1.046e-010  1.029e-010    -9.981    -9.988    -0.007     (0)
Mg            2.057e-005
   Mg+2           2.053e-005  1.927e-005    -4.688    -4.715    -0.028    -21.89
   MgSO4          2.629e-008  2.629e-008    -7.580    -7.580     0.000      5.84
   MgHCO3+        5.043e-009  4.963e-009    -8.297    -8.304    -0.007      5.46
   MgOH+          8.085e-012  7.958e-012   -11.092   -11.099    -0.007     (0)
   MgCO3          2.159e-012  2.159e-012   -11.666   -11.666     0.000    -17.09
Na            9.135e-005
   Na+            9.134e-005  8.990e-005    -4.039    -4.046    -0.007     -1.41
   NaSO4-         2.664e-009  2.622e-009    -8.574    -8.581    -0.007     18.40
   NaHCO3         1.113e-009  1.113e-009    -8.954    -8.954     0.000      2.13
   NaCO3-         1.997e-013  1.965e-013   -12.700   -12.707    -0.007     -0.63
   NaOH           1.035e-023  1.035e-023   -22.985   -22.985     0.000     (0)
O(0)          0.000e+000
   O2             0.000e+000  0.000e+000   -66.708   -66.708     0.000     30.40
S(-2)         3.204e-014
   H2S            3.162e-014  3.162e-014   -13.500   -13.500     0.000     37.16
   HS-            4.180e-016  4.113e-016   -15.379   -15.386    -0.007     20.59
   S-2            6.022e-024  5.650e-024   -23.220   -23.248    -0.028     (0)
S(6)          6.246e-006
   SO4-2          6.202e-006  5.819e-006    -5.207    -5.235    -0.028     13.95
   MgSO4          2.629e-008  2.629e-008    -7.580    -7.580     0.000      5.84
   CaSO4          9.678e-009  9.679e-009    -8.014    -8.014     0.000      7.50
   HSO4-          5.055e-009  4.974e-009    -8.296    -8.303    -0.007     40.26
   NaSO4-         2.664e-009  2.622e-009    -8.574    -8.581    -0.007     18.40
   KSO4-          1.046e-010  1.029e-010    -9.981    -9.988    -0.007     (0)
   CaHSO4+        5.684e-013  5.594e-013   -12.245   -12.252    -0.007     (0)
Si            1.046e-004
   H4SiO4         1.046e-004  1.046e-004    -3.980    -3.980     0.000     52.08
   H3SiO4-        1.783e-009  1.754e-009    -8.749    -8.756    -0.007     27.96
   H2SiO4-2       1.446e-017  1.357e-017   -16.840   -16.867    -0.028     (0)

------------------------------Saturation indices-------------------------------

       Phase               SI   log IAP   log K(298 K,   1 atm)

       Anhydrite        -5.99    -10.26   -4.28  CaSO4
       Aragonite        -6.62    -14.96   -8.34  CaCO3
       Calcite          -6.48    -14.96   -8.48  CaCO3
       CH4(g)          -14.87    -17.72   -2.84  CH4
       Chalcedony       -0.43     -3.98   -3.55  SiO2
       Chrysotile      -23.97      8.23   32.20  Mg3Si2O5(OH)4
       CO2(g)           -1.90     -3.36   -1.46  CO2   Pressure   0.0 atm, phi 1.000
       Dolomite        -12.51    -29.60  -17.09  CaMg(CO3)2
       Gypsum           -5.68    -10.26   -4.58  CaSO4:2H2O
```

```
H2(g)            -9.74    -12.84   -3.10  H2
H2O(g)           -1.50     -0.00    1.50  H2O
H2S(g)          -12.45    -20.44   -7.99  H2S
Halite           -9.57     -8.00    1.57  NaCl
O2(g)           -63.82    -66.71   -2.89  O2
Quartz            0.00     -3.98   -3.98  SiO2
Sepiolite       -16.91     -1.15   15.76  Mg2Si3O7.5OH:3H2O
Sepiolite(d)    -19.81     -1.15   18.66  Mg2Si3O7.5OH:3H2O
SiO2(a)          -1.27     -3.98   -2.71  SiO2
Sulfur           -8.70     -3.81    4.88  S
Sylvite         -10.45     -9.55    0.90  KCl
Talc            -21.13      0.27   21.40  Mg3Si4O10(OH)2
```

Appendix F Proposed Revised Florida Methods

F.1 Florida Method of Test for pH of Soil and Water, FM 5-550

Florida Method of Test for pH of Soil and Water

Designation: FM 5-550

1. SCOPE

   1.1. This method covers the determination of pH in soil and water using a pH/mV meter with automatic temperature compensation (ATC) and a combination electrode that includes a silver/silver chloride reference electrode, a glass bulb indicating electrode, and a thermocouple.

2. APPARATUS

   2.1. pH Meter and Electrode System: Portable or benchtop pH/mV meter with automatic temperature compensation (ATC) and accuracies for mV, the greater of ± 0.2 mV or ± 0.05%; for pH, ± 0.002 pH units; for temperature, ± 0.3°C, or better; a display of calibration data including %slope and offset; and a refillable double-junction 3-in-1 combination electrode that includes a silver/silver chloride ($Ag/AgCl_2$) reference electrode, glass bulb indicating electrode, and thermocouple with pH/ATC connectors that match the meter inputs, capable of measuring 0 to 14 pH from -5°C to 100°C with a minimum resolution of 0.01 pH units (for example, Fisher Scientific pH/mV meter kit catalog #13-636-AB150).

   2.2. Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

   2.3. 100 and 250 mL beakers, wash bottle, glass stirring rods, 100-mL scoop, and delicate glass cleaning tissues.

3. REAGENTS

   3.1. Standard buffered solutions for pH 4, 7, and 10.

   3.2. Electrode filling solution and electrode storage solution (refer to electrode manual).

3.3. Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

4. SAMPLES

4.1. Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for gathering samples. Excessive moisture should be avoided by sampling from an area that has been allowed to gravity drain for a short time. If the soil sample has excess free moisture, place approximately 2.2 pounds (1 kg) of the soil on top of a suitable sieve and cover with plastic. Allow the sample to drain for a minimum of one hr. This step may be performed in the lab prior to testing. If the soil sample is obtained from a heap that has been sitting for a long time, take the sample from a depth below the weathered surface where the moisture content appears to have stabilized. Avoid taking the sample from near a weathered soil surface. If sampling from ground level, remove top 12” (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but excess water should not be included with the sample. Soil samples should be placed in plastic or plastic-lined bags. Squeeze the bag down snugly around the sample and seal tightly to minimize contact with air.

4.2. Water Sampling: Water samples should be obtained from the main channel of rivers and streams. Sampling from other bodies of water such as lakes or ponds should be obtained from areas conducive to the capture of representative samples. Care should be observed not to sample from stagnant or pooled water, unless a structure will be placed in such an area. Sample the water just below the surface to alleviate introduction of floating debris, i.e. leaves, sticks, foam or trash. Fill the sample container to the top to eliminate introducing air into the sample and tightly seal the lid. The sample container shall be clean, at least 1 quart (1 liter) in size, and be either glass or plastic with an airtight lid. When possible, submerge the sample container below the surface of the water to completely fill and secure lid underwater.

4.3. Field Measurement of Soil pH: Fill a 250-mL beaker to the 100-mL mark with soil from sample container and add 100 mL of dilution water. Break up any clumps of soil. Stir thoroughly the soil and water mixture for ~20 seconds every 10 minutes over a 30-minute period. Continue with test procedure from Section 6.1.

4.4. Transporting the samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.

4.5. Storing Samples: If samples need to be stored, store water and soil samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Analyze samples within seven (7) days.

5. SAMPLE PREPARATION

5.1. Preparation of Water: Allow test sample to reach room temperature.

5.2. Preparation of Soil: Allow the soil sample and dilution water to reach room temperature. Place 100 g of sample in a 250 mL beaker and then add 100 mL of dilution water. Break up any clumps of soil. Stir thoroughly the soil and water mixture for ~20 seconds every 10 minutes over a 30-minute period.

6. TEST PROCEDURE

6.1. Calibration of pH Meter and Electrode System: Pour ~50 mL of pH 4, pH 7, and pH 10 standard buffer solutions into separate 100-mL beakers and allow solutions to reach room temperature prior to calibration (Note 1). Remove pH electrode from storage solution, rinse with dilution water and blot or dab dry with tissue, uncover the fill hole, then place in pH 7 buffer solution for ~10 minutes prior to calibration. Calibrate the pH/mV meter and 3-in-1 combination electrode with three standard buffers according to the directions in the manufacturer's instruction manual. When the calibration is complete, record the calibration slope in %, offset in mV, and buffer temperature in °C (Note 2). The slope must be within 95% to 102%, the offset within ± 10 mV, and the buffer temperatures within 25 ± 5°C; if otherwise, follow the instruction manual to clean, fill, equilibrate, re-calibrate, re-activate, or replace the electrode so that the slope, offset, and temperatures are within these values.

6.2. Care of Electrode: Check the electrode filling solution and keep filled to the fill hole. Between any two pH measurements, rinse electrode with dilution water and blot or dab the electrode tip dry with a delicate glass tissue (Note 3).

6.3. Check of Calibration: Check the calibration by measuring the pH of each of the standard buffers. The measured pH should be within 0.05 pH units of the buffer pH at the test temperature. Buffer pH versus test temperature data are typically tabulated on the buffer bottle. If the measured pH is outside 0.05 pH units of the buffer pH at test temperature, take corrective steps and re-calibrate the electrode (Note 4).

6.4. Determination of pH: Insert the pH electrode in the buffer, water or soil sample such that the portion of the electrode that contains the glass bulb, thermocouple, and liquid junction is submersed, typically about ½" (1.3 cm) of the electrode tip. Do not immerse the electrode to a depth greater than the electrode's internal reference solution, as the sample may penetrate into and contaminate the reference solution. Very gently stir the electrode in the sample (or alternately, gently move the sample beaker beneath the electrode) to assure a pH representative of the bulk solution (Note 5). Wait until the meter's stable reading indicator stays on for 10 seconds or longer (Note 6). Remove the electrode from the sample, rinse the tip with dilution water and blot or dab dry, and return the electrode to the sample for a second pH measurement. Wait until the meter's stable reading indicator stays on for 10 seconds or longer. Record the pH to the nearest hundredth pH units and sample temperature to the nearest tenth °C, for example, pH 7.00 @ 25.1°C. After the second reading, return the pH electrode to the pH 7 buffer and check that the electrode is still within calibration.

6.5. Storage of Electrode (Note 7): Store the pH electrode overnight or longer in its storage bottle either in the electrode storage solution with the fill hole open in pH 4 or 7 buffer with the fill hole closed. Do not store in dilution water as this will have an adverse effect on electrode performance. Tap water or standard buffer solutions are appropriate for short-term electrode storage.

Note 1: Always use fresh buffers for electrode calibration.

Note 2: For some meters, the slope and offset are presented separately for two buffers (for example, pH 4 and pH 7, or pH 7 and pH 10). Record the slope and offset for the range that includes the sample pH.

Note 3: With some 3-in-1 combination electrodes, the narrow space between the glass bulb and the temperature sensor traps liquid, whether buffer, sample, or dilution water. This trapped liquid can be transferred into the sample and may affect the pH reading.

Note 4: If after a sample pH measurement the calibration check fails, suspect a partially clogged liquid junction on the electrode. Add electrode filling solution to flush the liquid junction, and then re-check calibration.

Note 5: Ideally, once the pH reading has stabilized, the reading will not change whether gently stirred or unstirred. For low ionic strength solutions, however, the pH may not stabilize if stirred. If the pH reading does not stabilize after ~ 5 min with gentle stirring, obtain and record a stable reading with no stirring.

Note 6: Disable the "hold" feature of the pH meter.

Note 7: Store the electrode in accordance with manufacturer’s instructions if different from this section.

7. PRECISION AND BIAS

7.1. Bias: Single-operator, single laboratory bias for this method using an Accumet meter/electrode AB150/13-620-631 was evaluated at 20°C with repeated measures of each six aqueous standards ranging from pH 5.00 to pH 9.00. The average bias was -0.01 pH units.

7.2. Reproducibility: For two test materials, multi-laboratory standard deviations of a single test result were dependent on soil pH (Table 1). For materials of similar pH, the results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than the pH units shown in column labeled “Acceptable Range of Two Results.”

Table 1 Multi-Laboratory Precision for FM 5-550 pH

Material	Average, pH units	Standard Deviation, pH units	Acceptable Range of Two Results
Sand (A-3)	7.76	0.32	0.91
Sand (A-3)	5.11	0.15	0.42

F.2 Florida Method of Test for Minimum Resistivity of Soil and Water, FM 5-551

Florida Method of Test for Minimum Resistivity of Soil and Water

Designation: FM 5-551

1. SCOPE

1.1 This method covers the laboratory determination of resistivity of soil and water using a soil resistance meter and soil box.

2. APPARATUS

2.1 Resistivity Meter: Any four-pin terminal, null-balancing ohmmeter or multimeter capable of four-wire resistance measurements from one to one million ohms, either analog or digital (as examples, resistivity meters MC Miller Model 400A, Nilsson Model 400, and Tinker & Rasor Model SR-2).

2.2 Soil Box: Designed such that the cross-sectional area (cm^2) of the sample, with the box filled level, divided by the distance (cm) between the pins is equal to 1 cm (for example, MC Miller catalog #37008).

2.3 Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

2.4 Other: Test leads, thermometer, flat spatula, mixing spoon, large non-corrosive (glass, plastic, or stainless steel) bowl for mixing, 100-mL graduated cylinder, squeeze bottle for cleaning, and disposable nitrile gloves.

3. REAGENTS

3.1 Conductivity standard, sodium chloride, 250 µS/cm (for example, Fisher Scientific catalog #22366032).

3.2 Distilled or deionized water (hereafter referred to as dilution water) with a resistivity of 200,000 ohm-cm or greater (Note 1).

Note 1: Deionized or distilled water stored in containers that are not airtight will over time absorb ions from acidic and basic gases in the atmosphere. Absorbed ions will lower the water’s resistivity.

4. SAMPLES

4.1 Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for gathering samples. Excessive moisture should be avoided by sampling from an area that has been allowed to gravity drain for a short time. If the soil sample has excess free moisture, place approximately 2.2 pounds (1 kg) of the soil on top of a suitable sieve and cover with plastic. Allow the sample to drain for one hr. This step may be performed in the lab prior to testing. If the soil sample is obtained from a heap that has been sitting for a long time, take the sample from a depth below the weathered surface where the moisture content appears to have stabilized. Avoid taking the sample from near a weathered soil surface. If sampling from ground level, remove top 12” (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but excess water should not be included with the sample. Soil samples should be placed in plastic or plastic-lined bags. Squeeze the bag down snugly around the sample and seal tightly to minimize contact with air.

4.2 Water Sampling: Water samples should be obtained from the main channel of rivers and streams. Sampling from other bodies of water such as lakes or ponds should be obtained from areas conducive to the capture of representative samples. Care should be observed not to sample from stagnant or pooled water unless a structure will be placed in such an area. Sample the water just below the surface to alleviate introduction of floating debris such as leaves, sticks, foam or trash. Fill the sample container to the top to eliminate introducing air into the sample and tightly seal the lid. The sample container shall be clean, at least 1 quart (1 liter) in size, and be either glass or plastic with an airtight lid. When possible, submerge the sample container below the surface of the water to completely fill and secure lid underwater.

4.3 Transporting the Samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.

4.4 Storing Samples: Store water samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Analysis of a soil sample “as received” is preferred. If, however, soil samples cannot be analyzed within ~ 1 day of receipt, dry soil samples per Section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days.

5. SAMPLE PREPARATION

5.1 Preparation of Water: Allow test sample to reach room temperature.

5.2 Preparation of Soil:

A. Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 1,200 g.

B. Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 1,200 g.

6. TEST PROCEDURE

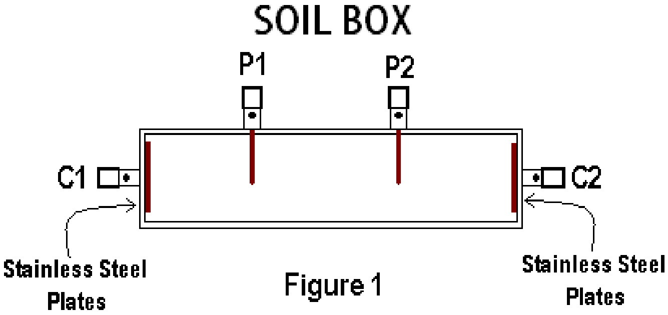

Figure 1

6.1 Equipment Set-up: Rinse the soil box, mixing bowl, and utensils with dilution water before starting and after completion of each test. Follow the manufacturer's instructions for properly connecting the test leads between the meter and the soil box. A standard soil box will have plates for application of current at both ends and a pair of electrode pins for reading potential evenly spaced between the plates (Figure 1).

6.2 Determine Resistivity of "As-Received" Soil: If an "as received" soil resistivity is requested, bring the soil sample and dilution water to room temperature. Place 1,000 g of "as-received" soil sample into a large bowl. Remove any debris (such as grass, roots, sticks or rocks, etc.). Fill the soil box to the top with the soil sample, taking care to fill any voids, and strike off any excess soil on the top of soil box. Connect the soil box to the resistivity meter as instructed in the manufacturer's instruction manual and determine the soil resistivity. Record the "as-received" resistivity in ohm-cm. Proceed to Section 6.3 to determine minimum resistivity.

6.3 Determine Minimum Resistivity of "As-Received" or of Dried, Sieved Soil: Bring the soil sample and dilution water to room temperature. Place 1,000 g of soil sample into a large bowl.

6.4 Add 100 mL of dilution water to the soil sample and mix thoroughly (Note 2).

6.5 Fill the soil box to the top with the soil sample, taking care to fill any voids, and strike off any excess soil on the top of soil box. Connect the soil box to the resistivity meter as instructed in the manufacturer's instruction manual and determine the soil resistivity. Record the total volume of water used in mL and the resistivity in ohm-cm. Place soil sample back into mixing bowl (Note 3).

6.6 Repeat steps 6.4 and 6.5. The measured resistivity should decrease. When the resistivity of the soil sample begins to increase, record the total volume of water used in mL and the higher resistivity, and measure and record the temperature in °C of the sample in the soil box.

6.7 Record the lowest resistivity obtained as the minimum resistivity and the temperature of the sample. Report the minimum resistivity in ohm-cm and the temperature in °C, for example, 3,000 ohm-cm @ 25°C.

6.8 Determine Resistivity of a Small Soil Sample: If soil resistivity is requested for a sample that is less than 1,000 g, complete steps 6.4 and 6.5 using increments of 10% water instead of 100 mL (Note 4).

Note 2: In some soils, even a trace amount of salt will affect the resistivity reading. Avoid transferring salt from hands to sample. For soils that are difficult to mix, wear disposable gloves and mix soil with gloved hands.

Note 3: In many cases the minimum resistivity will occur after soil slurry is formed. As water is added, mix thoroughly the soil slurry and pour the water from the slurry into the box until the box is filled. If the water alone cannot fill the soil box, add enough of the remaining soil to completely fill the box.

Note 4: A sample size of less than 1,000 g is not appropriate for select backfill (FDOT material 092L).

7. BEST PRACTICES

7.1 Determine Resistivity of Water: Refer to the manufacturer’s operation manual for determining resistivity.

7.2 Determine Resistivity of Conductivity Standard: Test the conductivity standard at least once per quarter and after the resistivity meter has undergone repair or replacement. Bring the conductivity standard to room temperature. Fill the soil box to the top with conductivity standard. Connect the soil box to the resistivity meter as instructed in the manufacturer’s instruction manual and verify that the conductivity standard resistivity is 4,000 ohm-cm @ 25°C. Refer to Table 1 for the conductivity of the standard for testing at temperatures between 20°C and 30°C. Record the conductivity standard resistivity in ohm-cm and the measurement temperature in °C. If the resistivity at measurement temperature is outside ±5%, troubleshoot and correct the problem, then re-test. Rinse the soil box well with dilution water after testing the conductivity standard.

Table 1 Temperature-Dependence of a 250 μS/cm NaCl Conductivity Standard

Temperature, °C	Resistivity, ohm-cm
20	4,440
21	4,350
22	4,250
23	4,170
24	4,080
25	4,000
26	3,920
27	3,850
28	3,780
29	3,710
30	3,650

8. PRECISION AND BIAS

8.1 Bias: Single-operator, single laboratory bias for this method was evaluated using a Nilsson Model 400 analog meter and a McMiller 280-mL soil box and repeated measures of two aqueous standards with resistivities at 25°C of 2,000 ohm-cm and 4,000 ohm-cm. After correcting for measurement temperatures in the range of 21°C to 23°C, average biases were -30 ohm-cm (-1.3%) for the 2,000 ohm-cm standard and 30 ohm-cm (0.7%) for the 4,000 ohm-cm standard. With no correction for temperature, average biases were 100 ohm-cm (5%) for the 2,000 ohm-cm standard and 300 ohm-cm (7%) for the 4,000 ohm-cm standard.

8.2 Reproducibility: For two test materials, multi-laboratory standard deviations of a single test results were dependent on soil minimum resistivity (Table 2). For materials with similar minimum resistivity, the results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than the ohm-cm shown in the column labeled “Acceptable Range of Two Results.”

Table 2 Multi-Laboratory Precision for FM 5-551 Minimum Resistivity

Material	Average, ohm-cm	Standard Deviation, ohm-cm	Acceptable Range of Two Results
Sand (A-3)	12,200	1,090	3,090
Sand (A-3)	2,310	430	1,230

F.3 Florida Method of Test for Chloride in Soil and Water, FM 5-552

Florida Method of Test for Chloride in Soil and Water

Designation: FM 5-552

1. SCOPE

1.1 This method covers the determination of chlorides in soil and water using either a screening approach based on a chloride reagent system or an analytical approach as found in the Standard Methods for the Examination of Water and Wastewater, Section 4500-Cl$^-$ B or Section 4110 B (SMEWW).

1.2 Both the screening and analytical approaches use a silver nitrate titration of a sample that is amended with a potassium chromate. Silver combines first with chloride and then with chromate in a mixture of the two. Both silver chloride and silver chromate are relatively insoluble in water but silver chromate is a brown-red crystal and its appearance in the sample marks the titration endpoint.

2. APPARATUS

2.1 Chloride Reagent System: Chloride Low Range Test Kit Model 8-P, 5-400 ppm (Hach catalog #144001) and Chloride High Range Test Kit Model CD-51 (Hach catalog #208601), or equivalent, may be used for chloride determinations. For the Hach Model 8-P test kit, additional glass mixing bottles with a 23-mL mark are needed (for example, Hach catalog #232706). Alternatively, the laboratory instruments referred to in the SMEWW may be used for chloride determination.

2.2 Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

2.3 Vacuum Filtration System: A vacuum filtration system is required. Such as system includes a vacuum pump, 0.25” (6 mm) inner diameter flexible vacuum hose, 300-mL filter funnel/holder for a 47-mm diameter filter, and a 1-liter side arm vacuum filtration flask or similar.

2.4 Other: Whatman 41 filter paper (or equivalent), glass or plastic funnel, two or more 500-mL Erlenmeyer flasks, 47-mm diameter 0.45-micron pore size mixed cellulose ester (MCE) membrane filters, 0.10-g measuring spoon, small ceramic dish, a transfer pipette (variable from 0.100 to 1.000

mL, capable of delivering increments of 0.01 mL) and tips, 100-mL graduated cylinder, and disposable nitrile gloves.

3. REAGENTS

3.1 Potassium dichromate ($K_2Cr_2O_7$), sodium bicarbonate and silver nitrate ($AgNO_3$) titrant are required for the chloride test kit (Note 1). The potassium dichromate and sodium bicarbonate are supplied as Chloride 2 powder pillows (for example, Hach catalog #105766). For the SMEWW method, reagent purchasing and preparation information is provided in the method procedures.

3.2 Chloride standard solution, 1,000 ppm (mg/L) as Cl^-, NIST-traceable.

3.3 Ferric sulfate, hydrated reagent grade (for example, Fisher Scientific catalog #S25322 or #S25322A).

3.4 Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

Note 1: Potassium chromate and silver nitrate are hazardous materials. Refer to the chemical safety data sheets (SDS) regarding the safe storage, handling, and disposal of these hazardous materials. Dispose of hazardous material in accordance with federal, state, and local mandates.

4. SAMPLES

4.1 Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for gathering samples. Excessive moisture should be avoided by sampling from an area that has been allowed to gravity drain for a short time. If the soil sample has excess free moisture, place approximately 2.2 pounds (1 kg) of the soil on top of a suitable sieve and cover with plastic. Allow the sample to drain for a minimum of one hr. This step may be performed in the lab prior to testing. If the soil sample is obtained from a heap that has been sitting for a long time, take the sample from a depth below the weathered surface where the moisture content appears to have stabilized. Avoid taking the sample from near a weathered soil surface. If sampling from ground level, remove top 12” (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but excess water should not be included with the sample. Soil samples should be placed in plastic or plastic-lined bags. Squeeze the bag down snugly around the sample and seal tightly to minimize contact with air.

4.2 Water Sampling: Water samples should be obtained from the main channel of rivers and streams. Sampling from other bodies of water such as lakes or ponds should be obtained from areas conducive to the capture of representative samples. Care should be observed not to sample from stagnant or pooled water, unless a structure will be placed in such an area. Sample the water just below the surface to alleviate introduction of floating debris such as leaves, sticks, foam or trash. Fill the sample container to the top to eliminate introducing air into the sample and tightly seal the lid. The sample container shall be clean, at least 1 quart (1 liter) in size, and be either glass or plastic with an airtight lid. When possible, submerge the sample container below the surface of the water to completely fill and secure lid underwater.

4.3 Transporting the samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.

4.4 Storing Samples: Store water samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Dry soil samples without delay per Section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days.

5. SAMPLE PREPARATION

5.1 Preparation of Water: Allow test sample to reach room temperature. If water sample contains suspended solids or color, gravity filter the water through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size MCE membrane filter.

5.2 Preparation of Soil:

A. Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at 140°F (60°C) for approximately four hr or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

B. Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

5.3 Preparation of Soil Extract: Place 100 grams of dried soil in a 500 mL Erlenmeyer flask (Note 2). Add 300 mL of dilution water, stopper, and shake vigorously for 20 seconds. Let stand for one hr and repeat agitation. Let stand for a minimum of 12 hr.

A. Suspended particles (turbidity) or color may interfere with the chloride determination. If the extract is cloudy or colored due to the suspension of fine particles, add ferric sulfate. Dissolve in a small ceramic dish ~0.10 g of ferric sulfate into 1 mL of water and pipette the dissolved ferric sulfate into the extract. Allow the sample to stand for three to four hr as the suspended particles settle.

B. Filter by gravity the soil extract through a Whatman 41 filter (or equivalent) into a 500-mL Erlenmeyer flask. Slowly decant into the filter the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping.

C. Filter by vacuum the soil extract through a 0.45-micron pore size membrane filter (Note 3) into a clean 1-liter vacuum filtration flask; repeat if necessary to get a clear extract.

Note 2: Prepare separate soil extracts for sulfate and chloride analyses. If after 12 hr of settling the both extracts are clear enough to filter, only one of two extracts needs to be filtered for both sulfate and chloride analysis.

Note 3: The MCE membrane filter is white; spacers are blue.

6. TEST PROCEDURE

6.1 Low Range: For the SMEWW analytical approach or an equivalent test kit, follow the kit instructions and include preparation and testing of a blank and 30-ppm check standard. For the Hach Model 8-P chloride test kit (5-400 ppm), follow these instructions:

A. Check the Reagents: Check that the silver chloride titrant and Chloride 2 Indicator powder pillows have not reached their expiration date.

B. Prepare a Reagent Blank: Fill one mixing bottle with dilution water to the 23-mL mark. Prepare a blank at least once per day on days in which samples are tested. Prepare a 30 mg/L (30 ppm) Check Standard: Add to a second mixing bottle 0.690 g of 1,000 mg/L chloride standard solution and fill with dilution water to the 23-mL mark.

C. Prepare a check standard at least once per day on days in which samples are tested.

D. Prepare a Water Sample or Soil Sample Extract: Fill a third mixing bottle with the water sample or soil sample extract to the 23-mL mark.

E. Determine the Blank Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the blank. Gently swirl the bottle to achieve a uniform yellow color. Add one drop of 0.0493 N silver nitrate to the blank and gently swirl the bottle to mix. Each drop is equal to ~5 mg/L (5 ppm) of chloride (Note 4). With one drop of silver nitrate the color of the blank should turn from yellow to red-brown; this red-brown color will serve as a guide (Note 5). If two or more drops of silver nitrate are necessary to titrate the dilution water to a red-brown color, then either the dilution water is contaminated with chloride or the titrant has gone bad (Notes 6 and 7).

Sample Calculation: 1 drop x 5 ppm/drop = 5 ppm per blank

F. Determine the Check Standard Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the check standard. Add one drop at a time of 0.0493 N silver nitrate and gently swirl the bottle to mix. The check standard should turn from yellow to red-brown after the addition of 6 to 8 drops. Record the total number of drops and subtract from this number one drop for the blank. Multiply the net number of drops by 5 ppm per drop. The check standard concentration should fall between 25 ppm and 35 ppm. If the concentration is less than 25 ppm or greater than 35 ppm the volume of added chloride standard or the drop size of silver nitrate may be off; otherwise the concentrations of either the chloride check standard or the silver nitrate titrant may be off. In either case, prepare a new check standard and re-test.

Sample Calculation: 7 drops x 5 ppm/drop = 35 ppm – 5 ppm blank = 30 ppm for check standard

G. Determine the Water Sample or Soil Sample Extract Chloride Concentration (0-60 ppm): Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the water sample or soil sample extract. Gently swirl the bottle to achieve a uniform yellow color. Add one drop at a time of 0.0493 N silver nitrate until the color of the extract changes from yellow to red-brown. Record the total number of drops and multiply each drop by 5 ppm of chloride per drop, then subtract from this concentration the 5 ppm of chloride for the blank. If this result is zero, record that the chloride concentration of the sample as below detection. Otherwise, multiply the chloride concentration by the dilution factor, which may be 1 for a water sample but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report this concentration in ppm.

Sample Calculation: 3 drops x 5 ppm/drop = 15 ppm – 5 ppm blank = 10 ppm x 3 dilution factor for soil extract = 30 ppm soil concentration

H. Determine the Water Sample or Soil Sample Extract Chloride Concentration (60-400 ppm): If the water sample or soil sample extract has not changed color after the addition of 13 drops (60 ppm), stop the titration. Prepare a new sample extract: fill a clean mixing bottle to the 10-mL mark. Add one drop at a time of 0.0493 N silver nitrate until the color of the extract changes from yellow to red-brown. Record the total number of drops and multiply each drop by 20 ppm of chloride per drop, then subtract from this concentration the 5 ppm of chloride for the blank. Otherwise, multiply the chloride concentration by the dilution factor, which may be 1 for a water sample but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report this concentration in ppm.

Sample Calculation: 3 drops x 20 ppm/drop = 60 ppm – 5 ppm blank = 55 ppm x 3 dilution factor for soil extract = 165 ppm soil concentration

6.2 High Range: If water or soil has a high chloride concentration (for example, seawater has a chloride concentration of ~19,000 ppm) use the Hach Model CD-51 chloride test kit (500-100,000) (or equivalent) and follow the kit instructions. For a check standard, fill the measuring tube with a 1000-ppm chloride standard and continue with the test instructions. The standard should be titrated from yellow to red-brown with 1-3 drops of 1.88-N silver nitrate titrant (500 ppm per drop). If more than 3 drops are required to titrate the standard, the titrant may be off.

6.3 Sample Dilution: Dilution of the water sample or soil sample extract will be necessary if the low range concentration is greater than 400 ppm. To dilute by a factor of 10, mix in a 100-mL graduated cylinder 10 mL of water sample or soil sample extract and 90 mL of dilution water. For the soil extract, multiply the chloride concentration by 3 for the initial dilution, then by 10 for the final dilution (factor of 30 for the total dilution).

Sample Calculation: 3 drops x 20 ppm/drop = 60 ppm – 5 ppm blank = 55 ppm x 30 dilution factor for soil extract = 1650 ppm soil concentration

Note 4: A dropper dispenses more accurately when held in a vertical position.

Note 5: White paper serves as a suitable background when observing solution colors.

Note 6: Silver nitrate degrades upon exposure to light and concentrates over time with evaporation. Keep opaque container tightly sealed and away from heat when not in use.

Note 7: If per FM 5-551, the resistivity of dilution water is greater than 200,000 ohm-cm, the concentration of chloride in dilution water is less than 5 ppm.

7. PRECISION AND BIAS

7.1 Bias: Single-operator, single laboratory bias for this method was evaluated using a Hach Chloride Low Range Test Kit Model 8-P, 5-400 ppm, and repeated measures of a 100-ppm aqueous standard, which was diluted by a factor of three to be in the target range of the test kit. Six replicate standards were tested, three with one lot number and three with a different lot number of Chloride 2 indicator. The average bias was -2.5 ppm (-2.5%).

7.2 Reproducibility: For a test material (sand, A-3) with an average chloride concentration of 66 ppm, the multi-laboratory standard deviation of a single test result has been found to be 12 ppm. Therefore, results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than 34 ppm.

F.4 Florida Method of Test for Sulfate in Soil and Water, FM 5-553

Florida Method of Test for Sulfate in Soil and Water

Designation: FM 5-553

1. SCOPE

1.1 This method covers the determination of sulfate in soil and water using either a screening approach based on a sulfate reagent system or an analytical approach as found in the Standard Methods for the Examination of Water and Wastewater, Section 4500-SO_4^{2-} E or Section 4110 B(SMEWW).

1.2 Both the screening and analytical approaches use the reaction of water-dissolved barium and sulfate to form an insoluble white precipitate of barium sulfate. The concentration (turbidity) of the precipitate is proportional to the sulfate concentration.

2. APPARATUS

2.1 Sulfate Reagent System: Sulfate, Pocket Colorimeter II Test Kit (Hach catalog #5870029), 2 to 70 mg/L, or equivalent, may be used for sulfate determinations. Additional glass sample cells with a 10-mL mark are needed (for example, Hach catalog #2427606). Alternatively, the apparatus referred to in the SMEWW may be used for sulfate determinations.

2.2 Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

2.3 Vacuum Filtration System: A vacuum filtration system is required. Such as system includes a vacuum pump, 0.25” (6 mm) inner diameter flexible vacuum hose, 300 mL filter funnel/holder for a 47-mm diameter filter, and a 1-liter side arm vacuum filtration flask or similar.

2.4 Other: Whatman 41 filter paper (or equivalent), glass or plastic funnel, two or more 500-mL Erlenmeyer flasks, 47-mm diameter 0.45-micron pore size mixed cellulose ester (MCE) membrane filters, transfer pipette (variable pipette from 0.100 to 1.000 mL, capable of delivering increments of 0.01 mL) and tips, timer (10 min, minimum), 100-mL graduated cylinder, and disposable nitrile gloves.

3. REAGENTS

3.1 Barium chloride ($BaCl_2$) (Note 1) and citric acid are required for the sulfate test kit. Barium chloride and citric acid are supplied as SulfaVer 4 powder pillows (for example, Hach catalog #21067-69). For the SMEWW method, reagent purchasing and preparation information is provided in the method procedures.

3.2 Sulfate standard solution, 1,000 ppm (mg/L) as SO_4^{2-}, NIST-traceable.

3.3 Hydrochloric acid (HCl) (Note 1), ~37%, reagent grade.

3.4 Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

Note 1: Barium chloride and hydrochloric acid are hazardous materials. Refer to the chemical material data safety (MSDS) sheets regarding the safe storage, handling, and disposal of these hazardous materials. Dispose of hazardous material in accordance with federal, state, and local mandates.

4. SAMPLES

4.1 Soil Sampling: Every effort should be made to obtain a soil sample that is representative of the bulk material. Use clean tools for gathering samples. Excessive moisture should be avoided by sampling from an area that has been allowed to gravity drain for a short time. If the soil sample has excess free moisture, place approximately 2.2 pounds (1 kg) of the soil on top of a suitable sieve and cover with plastic. Allow the sample to drain for a minimum of one hr. This step may be performed in the lab prior to testing. If the soil sample is obtained from a heap that has been sitting for a long time, take the sample from a depth below the weathered surface where the moisture content appears to have stabilized. Avoid taking the sample from near a weathered soil surface. If sampling from ground level, remove top 12” (30 cm) to eliminate vegetation and debris before sampling. The soil sample may be taken from underneath standing water, but excess water should not be included with the sample. Soil samples should be placed in plastic or plastic-lined bags. Squeeze the bag down snugly around the sample and seal tightly to minimize contact with air.

4.2 Water Sampling: Water samples should be obtained from the main channel of rivers and streams. Sampling from other bodies of water such as lakes or ponds should be obtained from areas conducive to the capture of representative samples. Care should be observed not to sample from stagnant or pooled water, unless a structure will be placed in such an area. Sample the water just below the surface to alleviate introduction of floating debris, i.e. leaves, sticks, foam or trash. Fill the sample container to the top to eliminate introducing air into the sample and tightly seal the lid. The sample container shall be clean, at least 1 quart (1 liter) in size, and be either glass or plastic with an airtight lid. When possible, submerge the sample container below the surface of the water to completely fill and secure lid underwater.

4.3 Transporting Samples: Maintain test samples in a cool dark area after sampling and during transport to the test facility.

4.4 Storing Samples: Store water samples at or below 39°C (4°C). Care should be taken to prevent freezing of the samples. Dry soil samples without delay per section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days.

5. SAMPLE PREPARATION

5.1 Preparation of Water: Allow test sample to reach room temperature. If water sample contains suspended solids or color, gravity filter the water sample through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size membrane filter.

5.2 Preparation of Soil:

A. Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

B. Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

C. Suspended particles (turbidity) or color will interfere with the sulfate determination. If the extract is cloudy or colored due to the suspension of fine particles, add a few (3-5) drops of hydrochloric acid. Allow the acidified extract to stand for one to four hr as the suspended particles settle (Note 3).

D. Filter by gravity the soil extract through a Whatman 41 filter into a 500-mL Erlenmeyer flask. Slowly decant into the filter the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping.

E. Filter by vacuum the soil extract through a 0.45-micron pore size membrane filter (Note 4) into a filtration flask; repeat if necessary to get a clear extract.

Note 2: Prepare separate soil extracts for sulfate and chloride analyses. If after 12 hr of settling the both extracts are clear enough to filter, only one of two extracts needs to be filtered for both sulfate and chloride analysis.

Note 3: More than a few drops of concentration hydrochloric acid will acidify the sample to less than pH 2, upon which the sample becomes hazardous material.

Note 4: The MCE membrane filter is white; spacers are blue.

6. TEST PROCEDURE

6.1 Low Range: For the SMEWW analytical approach, refer to the SMEWW step-by-step instructions. For the screening approach using the sulfate test kit (2-70 ppm), follow these instructions:

A. Check the Reagents and Glassware: Check that the SulfaVer 4 reagent powder pillows have not reached their expiration date. Check and clean as necessary glass sample cells so that cells are free of scratches, stains, deposits, or films that could affect light transmission through the glass.

B. Prepare a Reagent Blank: Fill one sample cell with dilution water to the 10-mL mark. Prepare a blank at least once per day on days in which samples are tested.

C. Prepare a 30 ppm Check Standard: Add to a second sample cell 0.30 g of 1,000-ppm (mg/L) sulfate standard solution and fill the sample cell to the 10-mL mark with dilution water. Prepare a check standard at least once per day on days in which samples are tested.

D. Prepare Water Sample or Soil Sample Extract (Sample) Blank and Sample: Fill the third and fourth cells with sample to the 10-mL mark. Use one of these cells as a blank to exclude (zero) any remaining turbidity or color.

E. React the Blanks, Standards, and Sample: Add one SulfaVer 4 powder pillow to each of these: the reagent blank, the 30 ppm check standard, and only one of the two cells that contain the sample. Cap all four sample cells and gently invert each cell 10 times to mix. Treat each of the four sample cells the same, as the mixing action may entrain air bubbles that will interfere with the measurement. Wipe the glass cells clean of fingerprints. Wait for a 5-minute reaction period with the sample cells undisturbed. Test the blanks, check standard, and samples within 10 minutes of adding the SulfaVer 4 reagent.

F. Select a Range for the Measurements (see Note 5 and Figure 1): Select a range on the photometer that gives the best results for the reagent lot number. To switch from Range 1 to Range 2, press the Menu key, then the Read key. Note the small arrow under the Range label. Use the same range for blanks, check standard, and samples.

G. Measure the Check Standard: Place the reagent blank into the sample cell holder and cap the holder. Press the photometer Zero key. After a few seconds the digital display should read 0. Remove the reagent blank and place the 30 ppm check standard into the sample cell holder and cap the holder. Press the photometer Read key. After a few seconds the digital display should read 30 (25 to 35). Record the reading. If the measured concentration is less than 25 ppm or greater than 35 ppm, check first for scratched or dirty glassware or a light leak through the cell holder; otherwise suspect the potency of SulfaVer 4 reagent; purity or volume of sulfate standard, or purity of dilution water. Troubleshoot and correct the problem before testing the sample extract

H. Measure the Sample Extract: Place the extract blank into the sample cell holder and cap the holder. Press the photometer Zero key. After a few seconds the digital display should read 0. Remove the extract blank and place the reacted extract into the sample cell holder and cap the holder. Press the photometer Read key. After a few seconds a reading will appear. If reading is 2 ppm or less, record reading as below detection. Otherwise, record the photometer reading and multiply the reading by 3 (dilution factor) to get the soil sulfate concentration. Record the dilution factor and the soil sulfate concentration in units of ppm.

6.2 Sample Dilution: Dilution of the test sample will be necessary if the sulfate concentration is greater than the maximum limit of the photometer (digital display will flash if reading is too high). To dilute by a factor of 10, mix in a 100-mL graduated cylinder 10 mL of sample and 90 mL of dilution water. Repeat steps 6.1 E, F, and H for the sample. For the soil extract, multiply the instrument reading by 3 for the initial dilution, then by 10 for the final dilution (factor of 30 for the total dilution).

Note 5: The Hach photometer includes a pre-programmed calibration curve on each range, Range 1 and Range 2. To check the built-in calibration curves, use a series of check standards from 0 to 70 ppm and plot the results. An example plot is shown below. Re-check the curves if the photometer is repaired or replaced, for each new lot of SulfaVer 4 powder pillows, and if a problem with the curve is suspected. Add in sequence to eight sample cells 0.00 g, 0.10 g, 0.20 g, 0.30 g, 0.40 g, 0.50 g, 0.60 g, and 0.70 g of 1,000 ppm (mg/L) sulfate standard solution. Fill each sample cell to the 10-mL mark with dilution water to obtain sulfate concentrations of 0, 10, 20, 30, 40, 50, 60, and 70 ppm. Test the calibration curve standards as described in the above procedures (6.1 E, F, and G). The Hach photometer also accepts a user-generated calibration curve as outlined in the instrument's instruction manual.

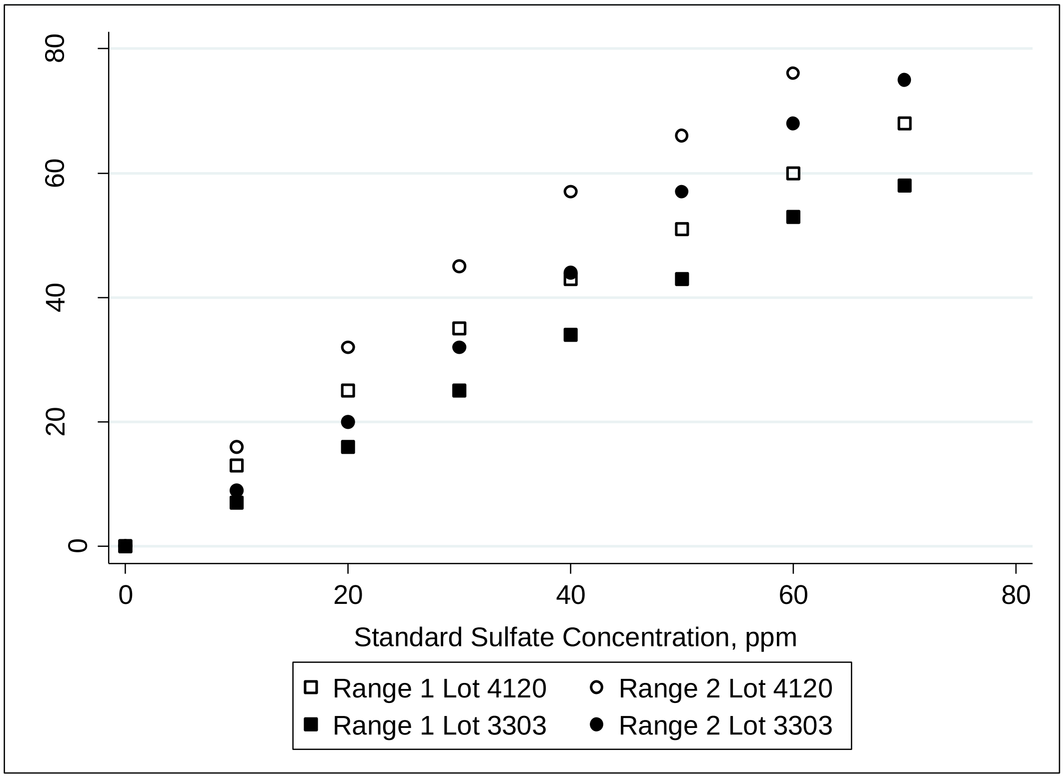

Figure 1. Plot of a Hach photometer response to sulfate standard solutions. For this photometer, the measured sulfate concentration was consistently higher on Range 2 than on Range 1. For both Range 1 and Range 2, moreover, the measured sulfate concentration was lower for SulfaVer 4 Lot 3303 than for Lot 4120, even though both lots were within their expiration dates.

7. PRECISION AND BIAS

7.1 Bias: Single-operator, single laboratory bias for this method was evaluated using a Hach Sulfate, Pocket Colorimeter II Test Kit and repeated measures of a 100-ppm aqueous standard, which was diluted by a factor of three to be in the target range of the test kit. Six replicate standards were tested, three with one lot number and three with a different lot number of SulfaVer 4 reagent. The average bias was -0.5 ppm (-0.5%).

7.2 Reproducibility: For at test material (sand, A-3) with an average sulfate concentration of 67 ppm, the multi-laboratory standard deviation of a single test result has been found to be 16 ppm. Therefore, results of two properly-conducted tests in different laboratories on the same material are not expected to differ by more than 45 ppm.

Appendix G Audit Checklists

G.1 Checklist for Florida Method of Test for pH of Soil and Water

APPARATUS

☐ pH Meter and Electrode System: Portable or benchtop pH/mV meter with automatic temperature compensation (ATC) and accuracies for mV: the greater of ± 0.2 mV or ± 0.05%, for pH: ± 0.002 pH units, and for temperature: ± 0.3°C, or better, a display of calibration data including %slope and offset; and a refillable double-junction 3-in-1 combination electrode that includes a silver/silver chloride ($Ag/AgCl_2$) reference electrode, glass bulb indicating electrode, and thermocouple with pH/ATC connectors that match the meter inputs, and capable of measuring 0 to 14 pH from -5°C to 100°C with a minimum resolution of 0.01 pH units (for example, Fisher Scientific pH/mV meter kit catalog #13-636-AB150).

☐ Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

☐ 100 and 250 mL beakers, wash bottle, glass stirring rods, 100-mL scoop, and delicate glass cleaning tissues.

REAGENTS

☐ Standard buffered solutions for pH 4, 7, and 10.

☐ Electrode filling solution and electrode storage solution (refer to electrode manual).

☐ Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

SAMPLES

☐ Storing Samples: If samples need to be stored, store water and soil samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Analyze samples within seven (7) days.

SAMPLE PREPARATION

☐ Preparation of Water: Allow test sample to reach room temperature.

☐ Preparation of Soil: Allow the soil sample and dilution water to reach room temperature. Place 100 g of sample in a 250 mL beaker and then add 100 mL of dilution water. Break up any clumps of soil. Stir thoroughly the soil and water mixture for ~20 seconds every 10 minutes over a 30-minute period.

TEST PROCEDURE

☐ Calibration of pH Meter and Electrode System: Pour ~50 mL of pH 4, pH 7, and pH 10 standard buffer solutions into separate 100-mL beakers and allow solutions to reach room temperature prior to calibration (Note 1). Remove pH electrode from storage solution, rinse with dilution water and blot or dab dry with tissue, uncover the fill hole, then place in pH 7 buffer solution for ~10 minutes prior to calibration. Calibrate the pH/mV meter and 3-in-1 combination electrode with three standard buffers according to the directions in the manufacturer's instruction manual. When the calibration is complete, record the calibration slope in %, offset in mV, and buffer temperature in °C (Note 2). The slope must be within 95% to 102%, the offset within ± 10 mV, and the buffer temperatures within 25 ± 5°C; if otherwise, follow the instruction manual to clean, fill, equilibrate, re-calibrate, re-activate, or replace the electrode so that the slope, offset, and temperatures are within these values.

☐ Care of Electrode: Check the electrode filling solution and keep filled to the fill hole. Between any two pH measurements, rinse electrode with dilution water and blot or dab the electrode tip dry with a delicate glass tissue (Note 3).

☐ Check of Calibration: Check the calibration by measuring the pH of each of the standard buffers. The measured pH should be within 0.05 pH units of the buffer pH at the test temperature. Buffer pH versus test temperature data are typically tabulated on the buffer bottle. If the measured pH is outside 0.05 pH units of the buffer pH at test temperature, take corrective steps and re-calibrate the electrode (Note 4).

☐ Determination of pH: Insert the pH electrode in the buffer, water or soil sample such that the portion of the electrode that contains the glass bulb, thermocouple, and liquid junction is submersed, typically about ½" (1.3 cm) of the electrode tip. Do not immerse the electrode to a depth greater than the electrode's internal reference solution, as the sample may penetrate into and contaminate the reference solution. Very gently stir the electrode in the sample (or alternately, gently move the sample beaker beneath the electrode) to assure a pH representative of the bulk solution (Note 5). Wait until the meter's stable reading indicator stays on for 10 seconds or longer (Note 6). Remove the electrode from the sample, rinse the tip with dilution water and blot or dab dry, and return the electrode to the sample for a second pH measurement. Wait until the meter’s stable reading indicator stays on for 10 seconds or longer. Record the pH to the nearest hundredth pH units and sample temperature to the nearest tenth °C, for example, pH 7.00 @ 25.1°C. After the second reading, return the pH electrode to the pH 7 buffer and check that the electrode is still within calibration.

☐ Storage of Electrode (Note 7): Store the pH electrode overnight or longer in its storage bottle either in the electrode storage solution with the fill hole open in pH 4 or 7 buffer with the fill hole closed. Do not store in dilution water as this will have an adverse effect on electrode performance. Tap water or standard buffer solutions are appropriate for short-term electrode storage.

Note 1: Always use fresh buffers for electrode calibration.

Note 2: For some meters, the slope and offset are presented separately for two buffers (for example, pH 4 and pH 7, or pH 7 and pH 10). Record the slope and offset for the range that includes the sample pH.

Note 3: With some 3-in-1 combination electrodes, the narrow space between the glass bulb and the temperature sensor traps liquid, whether buffer, sample, or dilution water. This trapped liquid can be transferred into the sample and may affect the pH reading.

Note 4: If after a sample pH measurement the calibration check fails, suspect a partially clogged liquid junction on the electrode. Add electrode filling solution to flush the liquid junction, and then re-check calibration.

Note 5: Ideally, once the pH reading has stabilized, the reading will not change whether gently stirred or unstirred. For low ionic strength solutions, however, the pH may not stabilize if stirred. If the pH reading does not stabilize after ~ 5 min with gentle stirring, obtain and record a stable reading with no stirring.

Note 6: Disable the “hold” feature of the pH meter.

Note 7: Store the electrode in accordance with manufacturer’s instructions if different from this section.

G.2 Checklist for Florida Method of Test for Minimum Resistivity of Soil and Water

APPARATUS

☐ Resistivity Meter: Any four-pin terminal, null-balancing ohmmeter or multimeter capable of four-wire resistance measurements from one to one million ohms, either analog or digital (as examples, resistivity meters MC Miller Model 400A, Nilsson Model 400, and Tinker & Rasor Model SR-2).

☐ Soil Box: Designed such that the cross-sectional area (cm^2) of the sample, with the box filled level, divided by the distance (cm) between the pins is equal to 1 cm (for example, MC Miller catalog #37008).

☐ Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

☐ Other: Test leads, thermometer, flat spatula, mixing spoon, large non-corrosive (glass, plastic, or stainless steel) bowl for mixing, 100-mL graduated cylinder, squeeze bottle for cleaning, and disposable nitrile gloves.

REAGENTS

☐ Conductivity standard, sodium chloride, 250 µS/cm (for example, Fisher Scientific catalog #22366032).

☐ Distilled or deionized water (hereafter referred to as dilution water) with a resistivity of 200,000 ohm-cm or greater (Note 1).

Note 1: Deionized or distilled water stored in containers that are not airtight will over time absorb ions from acidic and basic gases in the atmosphere. Absorbed ions will lower the water's resistivity.

SAMPLES

☐ Storing Samples: Store water samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Analysis of a soil sample "as received" is preferred. If, however, soil samples cannot be analyzed within ~ 1 day of receipt, dry soil samples per Section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days.

SAMPLE PREPARATION

☐ Preparation of Water: Allow test sample to reach room temperature.

☐ Preparation of Soil:

Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 1,200 g.

Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 1,200 g.

TEST PROCEDURE

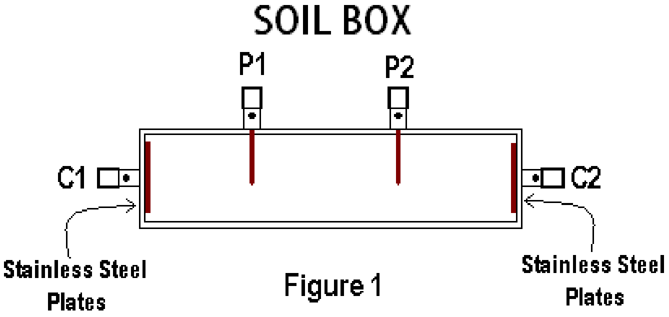

Figure 1

-

☐ Equipment Set-up: Rinse the soil box, mixing bowl, and utensils with dilution water before starting and after completion of each test. Follow the manufacturer's instructions for properly connecting the test leads between the meter and the soil box. A standard soil box will have plates for application of current at both ends and a pair of electrode pins for reading potential evenly spaced between the plates (Figure 1).

☐ Determine Resistivity of “As-Received” Soil: If an “as received” soil resistivity is requested, bring the soil sample and dilution water to room temperature. Place 1,000 g of “as-received” soil sample into a large bowl.

Remove any debris (such as grass, roots, sticks or rocks, etc.). Fill the soil box to the top with the soil sample, taking care to fill any voids, and strike off any excess soil on the top of soil box. Connect the soil box to the resistivity meter as instructed in the manufacturer's instruction manual and determine the soil resistivity. Record the "as-received" resistivity in ohm-cm. Proceed to Section 6.3 to determine minimum resistivity.

☐ Determine Minimum Resistivity of "As-Received" or of Dried, Sieved Soil: Bring the soil sample and dilution water to room temperature. Place 1,000 g of dried soil sample into a large bowl.

Add 100 mL of dilution water to the soil sample and mix thoroughly (Note 2).

Fill the soil box to the top with the soil sample, taking care to fill any voids, and strike off any excess soil on the top of soil box. Connect the soil box to the resistivity meter as instructed in the manufacturer's instruction manual and determine the soil resistivity. Record the total volume of water used in mL and the resistivity in ohm-cm. Place soil sample back into mixing bowl (Note 3).

Repeat steps 6.5 A and 6.5 B. The measured resistivity should decrease. When the resistivity of the soil sample begins to increase, record the total volume of water used in mL and the higher resistivity, and measure and record the temperature in °C of the sample in the soil box.

Record the lowest resistivity obtained as the minimum resistivity and the temperature of the sample. Report the minimum resistivity in ohm-cm and the temperature in °C, for example, 3,000 ohm-cm @ 25°C.

☐ Determine Resistivity of a Small Soil Sample: If soil resistivity is requested for a sample that is less than 1,000 g, complete steps 6.5 A and 6.5 B using increments of 10% water instead of 100 mL (Note 4).

Note 2: In some soils, even a trace amount of salt will affect the resistivity reading. Avoid transferring salt from hands to sample. For soils that are difficult to mix, wear disposable gloves and mix soil with gloved hands.

Note 3: In many cases the minimum resistivity will occur after soil slurry is formed. As water is added, mix thoroughly the soil slurry and pour the water from the slurry into the box until the box is filled. If the water alone cannot fill the soil box, add enough of the remaining soil to completely fill the box.

Note 4: A sample size of less than 1,000 g is not appropriate for select backfill (FDOT material 092L).

BEST PRACTICES

- ☐ Determine Resistivity of Water: Refer to the manufacturer’s operation manual for determining resistivity.

- ☐ Determine Resistivity of Conductivity Standard: Test the conductivity standard at least once per quarter and after the resistivity meter has undergone repair or replacement. Bring the conductivity standard to room temperature. Fill the soil box to the top with conductivity standard. Connect the soil box to the resistivity meter as instructed in the manufacturer’s instruction manual and verify that the conductivity standard resistivity is 4,000 ohm-cm @ 25°C. Refer to Table 1 for the conductivity of the standard for testing at temperatures between 20°C and 30°C. Record the conductivity standard resistivity in ohm-cm and the measurement temperature in °C. If the resistivity at measurement temperature is outside ±5%, troubleshoot and correct the problem, then re-test. Rinse the soil box well with dilution water after testing the conductivity standard.

Table 1 Temperature-Dependence of a 250 μS/cm NaCl Conductivity Standard

Temperature, °C	Resistivity, ohm-cm
20	4,440
21	4,350
22	4,250
23	4,170
24	4,080
25	4,000
26	3,920
27	3,850
28	3,780
29	3,710
30	3,650

G.3 Checklist for Florida Method of Test for Chloride in Soil and Water

APPARATUS

☐ Chloride Reagent System: Chloride Low Range Test Kit Model 8-P, 5-400 ppm (Hach catalog #144001) and Chloride High Range Test Kit Model CD-51 (Hach catalog #208601), or equivalent, may be used for chloride determinations. For the Hach Model 8-P test kit, additional glass mixing bottles with a 23-mL mark are needed (for example, Hach catalog #232706). Alternatively, the laboratory instruments referred to in the SMEWW may be used for chloride determination.

☐ Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

☐ Vacuum Filtration System: A vacuum filtration system is required. Such as system includes a vacuum pump, 0.25” (6 mm) inner diameter flexible vacuum hose, 300-mL filter funnel/holder for a 47-mm diameter filter, and a 1-liter side arm vacuum filtration flask or similar.

☐ Other: Whatman 41 filter paper (or equivalent), glass or plastic funnel, two or more 500-mL Erlenmeyer flasks, 47-mm diameter 0.45-micron pore size mixed cellulose ester (MCE) membrane filters, 0.10-g measuring spoon, small ceramic dish, a transfer pipette (variable from 0.100 to 1.000 mL, capable of delivering increments of 0.01 mL) and tips, 100-mL graduated cylinder, and disposable nitrile gloves.

REAGENTS

☐ Potassium dichromate ($K_2Cr_2O_7$), sodium bicarbonate and silver nitrate ($AgNO_3$) titrant are required for the chloride test kit (Note 1). The potassium dichromate and sodium bicarbonate are supplied as Chloride 2 powder pillows (for example, Hach catalog #105766). For the SMEWW method, reagent purchasing and preparation information is provided in the method procedures.

☐ Chloride standard solution, 1,000 ppm (mg/L) as Cl^-, NIST-traceable.

☐ Ferric sulfate, hydrated reagent grade (for example, Fisher Scientific catalog #S25322 or #S25322A).

☐ Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

Note 1: Potassium chromate and silver nitrate are hazardous materials. Refer to the chemical safety data sheets (SDS) regarding the safe storage, handling, and disposal of these hazardous materials. Dispose of hazardous material in accordance with federal, state, and local mandates.

SAMPLES

☐ Storing Samples: Store water samples at or below 39°F (4°C). Care should be taken to prevent freezing of the samples. Dry soil samples without delay per Section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days.

SAMPLE PREPARATION

☐ Preparation of Water: Allow test sample to reach room temperature. If water sample contains suspended solids or color, gravity filter the water through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size MCE membrane filter.

☐ Preparation of Soil:

Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at 140°F (60°C) for approximately four hr or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

☐ Preparation of Soil Extract: Place 100 grams of dried soil in a 500 mL Erlenmeyer flask (Note 2). Add 300 mL of dilution water, stopper, and shake vigorously for 20 seconds. Let stand for one hr and repeat agitation. Let stand for a minimum of 12 hr.

Suspended particles (turbidity) or color may interfere with the chloride determination. If the extract is cloudy or colored due to the suspension of fine particles, add ferric sulfate. Dissolve in a small ceramic dish ~0.10 g of ferric sulfate into 1 mL of water and pipette the dissolved ferric sulfate into the extract. Allow the sample to stand for one to four hr as the suspended particles settle.

Filter by gravity the soil extract through a Whatman 41 filter (or equivalent) into a 500-mL Erlenmeyer flask. Slowly decant into the filter the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping.

Filter by vacuum the soil extract through a 0.45-micron pore size membrane filter (Note 3) into a clean 1-liter vacuum filtration flask; repeat if necessary to get a clear extract.

Note 2: Prepare separate soil extracts for sulfate and chloride analyses. If after 12 hr of settling the both extracts are clear enough to filter, only one of two extracts needs to be filtered for both sulfate and chloride analysis.

Note 3: The MCE membrane filter is white; spacers are blue.

TEST PROCEDURE

☐ Low Range: For the SMEWW analytical approach or an equivalent test kit, follow the kit instructions and include preparation and testing of a blank and 30-ppm check standard. For the Hach Model 8-P chloride test kit (5-400 ppm), follow these instructions:

Check the Reagents: Check that the silver chloride titrant and Chloride 2 Indicator powder pillows have not reached their expiration date.

Prepare a Reagent Blank: Fill one mixing bottle with dilution water to the 23-mL mark. Prepare a blank at least once per day on days in which samples are tested.

Prepare a 30 mg/L (30 ppm) Check Standard: Add to a second mixing bottle 0.690 g of 1,000 mg/L chloride standard solution and fill with dilution water to the 23-mL mark. Prepare a check standard at least once per day on days in which samples are tested.

Prepare a Water Sample or Soil Sample Extract: Fill a third mixing bottle with the water sample or soil sample extract to the 23-mL mark.

Determine the Blank Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the blank. Gently swirl the bottle to achieve a uniform yellow color. Add one drop of 0.0493 N silver nitrate to the blank and gently swirl the bottle to mix. Each drop is equal to ~5 mg/L (5 ppm) of chloride (Note 4). With one drop of silver nitrate the color of the blank should turn from yellow to red-brown; this red-brown color will serve as a guide (Note 5). If two or more drops of silver nitrate are necessary to titrate the dilution water to a red-brown color, then either the dilution water is contaminated with chloride or the titrant has gone bad (Notes 6 and 7).

Sample Calculation: 1 drop x 5 ppm/drop = 5 ppm per blank

Determine the Check Standard Chloride Concentration: Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the check standard. Add one drop at a time of 0.0493 N silver nitrate and gently swirl the bottle to mix. The check standard should turn from yellow to red-brown after the addition of 6 to 8 drops. Record the total number of drops and subtract from this number one drop for the blank. Multiply the net number of drops by 5 ppm per drop. The check standard concentration should fall between 25 ppm and 35 ppm. If the concentration is less than 25 ppm or greater than 35 ppm the volume of added chloride standard or the drop size of silver nitrate may be off; otherwise the concentrations of either the chloride check standard or the silver nitrate titrant may be off. In either case, prepare a new check standard and re-test.

Sample Calculation: 7 drops x 5 ppm/drop = 35 ppm – 5 ppm blank = 30 ppm for check standard

Determine the Water Sample or Soil Sample Extract Chloride Concentration (0-60 ppm): Add one Chloride 2 Indicator powder pillow (potassium dichromate/sodium bicarbonate) to mixing bottle that contains the water sample or soil sample extract. Gently swirl the bottle to achieve a uniform yellow color. Add one drop at a time of 0.0493 N silver nitrate until the color of the extract changes from yellow to red-brown. Record the total number of drops and multiply each drop by 5 ppm of chloride per drop, then subtract from this concentration the 5 ppm of chloride for the blank. If this result is zero, record that the chloride concentration of the sample as below detection. Otherwise, multiply the chloride concentration by the dilution factor, which may be 1 for a water sample but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report this concentration in ppm.

Sample Calculation: 3 drops x 5 ppm/drop = 15 ppm – 5 ppm blank = 10 ppm x 3 dilution factor for soil extract = 30 ppm soil concentration

Determine the Water Sample or Soil Sample Extract Chloride Concentration (60-400 ppm): If the water sample or soil sample extract has not changed color after the addition of 13 drops (60 ppm), stop the titration. Prepare a new sample extract: fill a clean mixing bottle to the 10-mL mark. Add one drop at a time of 0.0493 N silver nitrate until the color of the extract changes from yellow to red-brown. Record the total number of drops and multiply each drop by 20 ppm of chloride per drop, then subtract from this concentration the 5 ppm of chloride for the blank. Otherwise, multiply the chloride concentration by the dilution factor, which may be 1 for a water sample but 3 to account for the initial dilution of a soil sample (100 grams of soil to 300 mL water). Report this concentration in ppm.

Sample Calculation: 3 drops x 20 ppm/drop = 60 ppm – 5 ppm blank = 55 ppm x 3 dilution factor for soil extract = 165 ppm soil concentration

☐ High Range: If water or soil has a high chloride concentration (for example, seawater has a chloride concentration of ~19,000 ppm) use the Hach Model CD-51 chloride test kit (500-100,000) (or equivalent) and follow the kit instructions. For a check standard, fill the measuring tube with a 1000-ppm chloride standard and continue with the test instructions. The standard should be titrated from yellow to red-brown with 1-3 drops of 1.88-N silver nitrate titrant (500 ppm per drop). If more than 3 drops are required to titrate the standard, the titrant may be off.

☐ Sample Dilution: Dilution of the water sample or soil sample extract will be necessary if the low range concentration is greater than 400 ppm. To dilute by a factor of 10, mix in a 100-mL graduated cylinder 10 mL of water sample or soil sample extract and 90 mL of dilution water. For the soil extract, multiply the chloride concentration by 3 for the initial dilution, then by 10 for the final dilution (factor of 30 for the total dilution).

Sample Calculation: 3 drops x 20 ppm/drop = 60 ppm – 5 ppm blank = 55 ppm x 30 dilution factor for soil extract = 1650 ppm soil concentration

Note 4: A dropper dispenses more accurately when held in a vertical position.

Note 5: White paper serves as a suitable background when observing solution colors.

Note 6: Silver nitrate degrades upon exposure to light and concentrates over time with evaporation. Keep opaque container tightly sealed and away from heat when not in use.

Note 7: If per FM 5-551, the resistivity of dilution water is greater than 200,000 ohm-cm, the concentration of chloride in dilution water is less than 5 ppm.

G.4 Checklist for Florida Method of Test for Sulfate in Soil and Water

APPARATUS

☐ Sulfate Reagent System: Sulfate, Pocket Colorimeter II Test Kit (Hach catalog #5870029), 2 to 70 mg/L, or equivalent, may be used for sulfate determinations. Additional glass sample cells with a 10-mL mark are needed (for example, Hach catalog #2427606). Alternatively, the apparatus referred to in the SMEWW may be used for sulfate determinations.

☐ Analytical Balance: An analytical balance with a capacity of 2,000 g or more and a resolution of 0.01 g or better.

☐ Vacuum Filtration System: A vacuum filtration system is required. Such as system includes a vacuum pump, 0.25" (6 mm) inner diameter flexible vacuum hose, 300 mL filter funnel/holder for a 47-mm diameter filter, and a 1-liter side arm vacuum filtration flask or similar.

☐ Other: Whatman 41 filter paper (or equivalent), glass or plastic funnel, two or more 500-mL Erlenmeyer flasks, 47-mm diameter 0.45-micron pore size mixed cellulose ester (MCE) membrane filters, transfer pipette (variable pipette from 0.100 to 1.000 mL, capable of delivering increments of 0.01 mL) and tips, timer (10 min, minimum), 100-mL graduated cylinder, and disposable nitrile gloves.

REAGENTS

☐ Barium chloride (BaCl2) (Note 1) and citric acid are required for the sulfate test kit. Barium chloride and citric acid are supplied as SulfaVer 4 powder pillows (for example, Hach catalog #21067-69). For the SMEWW method, reagent purchasing and preparation information is provided in the method procedures.

☐ Sulfate standard solution, 1,000 ppm (mg/L) as SO_4^{2-}, NIST-traceable.

☐ Hydrochloric acid (HCl) (Note 1), ~37%, reagent grade.

☐ Deionized or distilled water (dilution water) with a resistivity equal or greater than 200,000 ohm-cm.

Note 1: Barium chloride and hydrochloric acid are hazardous materials. Refer to the chemical material data safety (MSDS) sheets regarding the safe storage, handling, and disposal of these hazardous materials. Dispose of hazardous material in accordance with federal, state, and local mandates.

SAMPLES

- ☐ Storing Samples: Store water samples at or below 39°C (4°C). Care should be taken to prevent freezing of the samples. Dry soil samples without delay per section 5.2 and store dried soil at room temperature prior to analysis. Analyze samples within seven (7) days.

SAMPLE PREPARATION

- ☐ Preparation of Water: Allow test sample to reach room temperature. If water sample contains suspended solids or color, gravity filter the water sample through a Whatman 41 filter (or equivalent), and if necessary, vacuum filter the water sample through a 0.45-micron pore size membrane filter.

- ☐ Preparation of Soil:

  Loose Granular Soils: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

  Muck and Soils with Clay: Spread the sample in a thin layer on a clean tray and dry under ambient conditions until a constant mass is achieved, or dry in an oven at no higher than 140°F (60°C) for approximately four hr or until a constant mass is achieved. Using a rawhide mallet or other suitable device pulverize the sample and sieve through a No. 10 mesh (2 mm) sieve. Split the sample per ASTM C 702-98 to obtain approximately 400 g.

- ☐ Preparation of Soil Extract: Place 100 grams of dried soil in a 500-mL Erlenmeyer flask (Note 2). Add 300 mL of dilution water, stopper, and shake vigorously for 20 seconds. Let stand for one hr and repeat agitation. Let stand for a minimum of 12 hr.

  Suspended particles (turbidity) or color will interfere with the sulfate determination. If the extract is cloudy or colored due to the suspension of fine particles, add a few (3-5) drops of hydrochloric acid. Allow the acidified extract to stand for one to four hr as the suspended particles settle (Note 3).

  Filter by gravity the soil extract through a Whatman 41 filter into a 500-mL Erlenmeyer flask. Slowly decant into the filter the water layer followed by the soil slurry from the sample extract and allow the liquid to drain until the liquid stops dripping.

Filter by vacuum the soil extract through a 0.45-micron pore size membrane filter (Note 4) into a filtration flask; repeat if necessary to get a clear extract.

Note 2: Prepare separate soil extracts for sulfate and chloride analyses. If after 12 hr of settling the both extracts are clear enough to filter, only one of two extracts needs to be filtered for both sulfate and chloride analysis.

Note 3: More than a few drops of concentration hydrochloric acid will acidify the sample to less than pH 2, upon which the sample becomes hazardous material.

Note 4: The MCE membrane filter is white; spacers are blue.

TEST PROCEDURE

☐ Low Range: For the SMEWW analytical approach, refer to the SMEWW step-by-step instructions. For the screening approach using the sulfate test kit (2-70 ppm), follow these instructions:

Check the Reagents and Glassware: Check that the SulfaVer 4 reagent powder pillows have not reached their expiration date. Check and clean as necessary glass sample cells so that cells are free of scratches, stains, deposits, or films that could affect light transmission through the glass.

Prepare a Reagent Blank: Fill one sample cell with dilution water to the 10-mL mark. Prepare a blank at least once per day on days in which samples are tested.

Prepare a 30 ppm Check Standard: Add to a second sample cell 0.30 g of 1,000-ppm (mg/L) sulfate standard solution and fill the sample cell to the 10-mL mark with dilution water. Prepare a check standard at least once per day on days in which samples are tested.

Prepare Water Sample or Soil Sample Extract (Sample) Blank and Sample: Fill the third and fourth cells with sample to the 10-mL mark. Use one of these cells as a blank to exclude (zero) any remaining turbidity or color.

React the Blanks, Standards, and Sample: Add one SulfaVer 4 powder pillow to each of these: the reagent blank, the 30 ppm check standard, and only one of the two cells that contain the sample. Cap all four sample cells and gently invert each cell 10 times to mix. Treat each of the four sample cells the same, as the mixing action may entrain air bubbles that will interfere with the measurement. Wipe the glass cells clean of fingerprints. Wait for a 5-minute reaction period with the sample cells undisturbed. Test the blanks, check standard, and samples within 10 minutes of adding the SulfaVer 4 reagent.

Select a Range for the Measurements (see Note 5 and Figure 1): Select a range on the photometer that gives the best results for the reagent lot number. To switch from Range 1 to Range 2, press the Menu key, then the Read key. Note the small arrow under the Range label. Use the same range for blanks, check standard, and samples.

Measure the Check Standard: Place the reagent blank into the sample cell holder and cap the holder. Press the photometer Zero key. After a few seconds the digital display should read 0. Remove the reagent blank and place the 30 ppm check standard into the sample cell holder and cap the holder. Press the photometer Read key. After a few seconds the digital display should read 30 (25 to 35). Record the reading. If the measured concentration is less than 25 ppm or greater than 35 ppm, check first for scratched or dirty glassware or a light leak through the cell holder; otherwise suspect the potency of SulfaVer 4 reagent; purity or volume of sulfate standard, or purity of dilution water. Troubleshoot and correct the problem before testing the sample extract

Measure the Sample Extract: Place the extract blank into the sample cell holder and cap the holder. Press the photometer Zero key. After a few seconds the digital display should read 0. Remove the extract blank and place the reacted extract into the sample cell holder and cap the holder. Press the photometer Read key. After a few seconds a reading will appear. If reading is 2 ppm or less, record reading as below detection. Otherwise, record the photometer reading and multiply the reading by 3 (dilution factor) to get the soil sulfate concentration. Record the dilution factor and the soil sulfate concentration in units of ppm.

☐ Sample Dilution: Dilution of the test sample will be necessary if the sulfate concentration is greater than the maximum limit of the photometer (digital display will flash if reading is too high). To dilute by a factor of 10, mix in a 100-mL graduated cylinder 10 mL of sample and 90 mL of dilution water. Repeat steps 6.1 E, F, and H for the sample. For the soil extract, multiply the instrument reading by 3 for the initial dilution, then by 10 for the final dilution (factor of 30 for the total dilution).

Note 5: The Hach photometer includes a pre-programmed calibration curve on each range, Range 1 and Range 2. To check the built-in calibration curves, use a series of check standards from 0 to 70 ppm and plot the results. An example plot is shown below. Re-check the curves if the photometer is repaired or replaced, for each new lot of SulfaVer 4 powder pillows, and if a problem with the curve is suspected. Add in sequence to eight sample cells 0.00 g, 0.10 g, 0.20 g, 0.30 g, 0.40 g, 0.50 g, 0.60 g, and 0.70 g of 1,000 ppm (mg/L) sulfate standard solution. Fill each sample cell to the 10-mL mark with dilution water to obtain sulfate concentrations of 0, 10, 20, 30, 40, 50, 60, and 70 ppm. Test the calibration curve standards as described in the above procedures (6.1 E, F, and G). The Hach photometer also accepts a user-generated calibration curve as outlined in the instrument’s instruction manual.

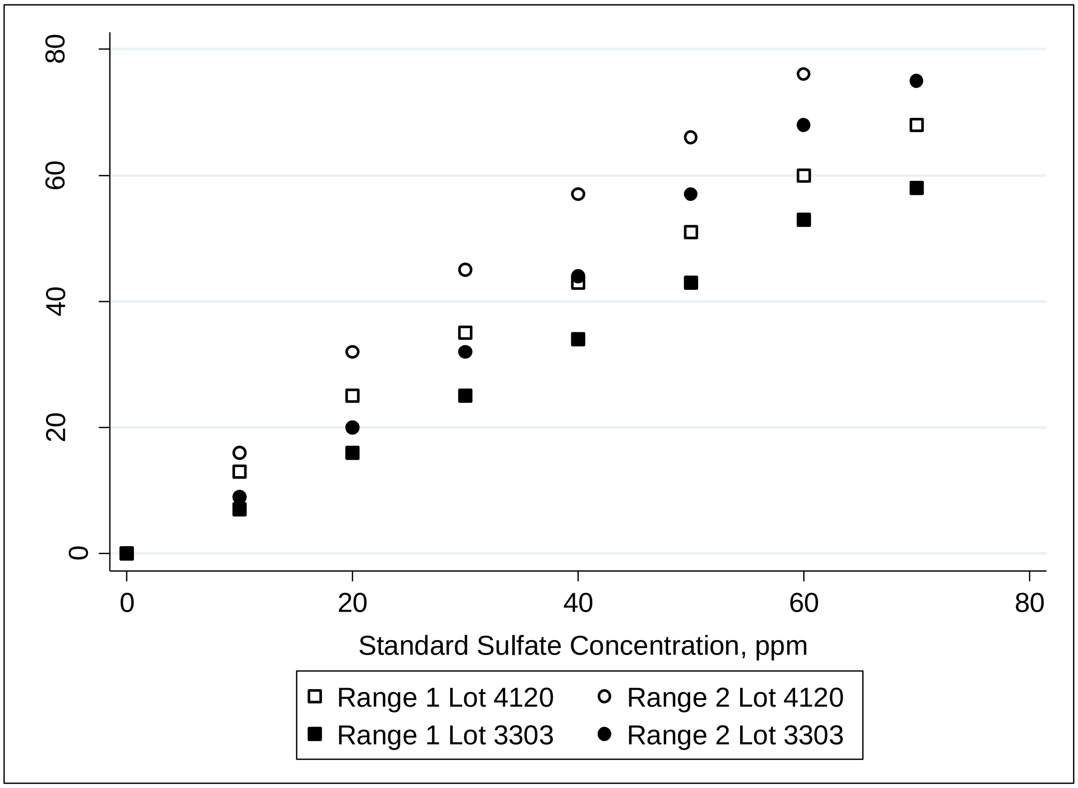

Figure 1. Plot of a Hach photometer response to sulfate standard solutions. For this photometer, the measured sulfate concentration was consistently higher on Range 2 than on Range 1. For both Range 1 and Range 2, moreover, the measured sulfate concentration was lower for SulfaVer 4 Lot 3303 than for Lot 4120, even though both lots were within their expiration dates.