Final Report

Title: Determination of Test Methods to Quantify the Effects of Organic and Inorganic Constituents in Silica Sand Used for Construction
FDOT Contract Number: BED31-977-30

Submitted to

The Florida Department of Transportation Research Center
605 Suwannee Street, MS 30 Tallahassee, FL 32399

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July 2026
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Prepared in cooperation with the State of Florida Department of Transportation and the U.S. Department of Transportation.

SI (MODERN METRIC) CONVERSION FACTORS (FROM FHWA)

Symbol	When You Know	Multiply By	To Find	Symbol
Length				
in	Inches	25.4	millimeters	mm
ft	Feet	0.305	meters	m
yd	Yards	0.914	meters	m
mi	Miles	1.61	kilometers	km
Area				
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
mi^2	square miles	2.59	square kilometers	km^2
Volume				
fl oz	fluid ounces	29.57	milliliters	mL
gal	Gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
Mass				
oz	Ounces	28.35	grams	g
lb	Pounds	0.454	kilograms	kg
Temperature (exact degrees)				
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
Force/Pressure				
psi	Pounds per square inch	6.895	kilopascals	kPa
kip	Kilopounds force	4.448	kilonewtons	k

TECHNICAL REPORT DOCUMENTATION

<table>
<tr><td colspan="2">1. Report No.</td><td>2. Government Accession No.</td><td colspan="2">3. Recipient's Catalog No.</td></tr>
<tr><td colspan="3" rowspan="2">4. Determination of Test Methods to Quantify the Effects of Organic and Inorganic Constituents in Silica Sand Used for Construction</td><td colspan="2">5. Report Date
July, 2026</td></tr>
<tr><td colspan="2">6. Performing Organization Code</td></tr>
<tr><td colspan="3">7. Author(s) Christopher C. Ferraro, Kyle A. Riding,
Ashish D. Patel, José Ignacio Dávila Gordillo, Timothy K. Mueller</td><td colspan="2">8. Performing Organization Report No.</td></tr>
<tr><td colspan="3" rowspan="2">9. Performing Organization Name and Address:
Department of Civil and Coastal Engineering
Engineering School of Sustainable Infrastructure & Environment
University of Florida
365 Weil Hall P.O. Box 116580
Gainesville, FL 32611-6580</td><td colspan="2">10. Work Unit No.</td></tr>
<tr><td colspan="2">11. Contract or Grant No.
BED31-977-30</td></tr>
<tr><td colspan="3" rowspan="2">12. Sponsoring Agency Name and Address
Florida Department of Transportation
605 Suwannee Street, MS 30
Tallahassee, FL 32399</td><td colspan="2">13. Type of Report and Period Covered: Final Report, June, 2024 – July, 2026</td></tr>
<tr><td colspan="2">14. Sponsoring Agency Code</td></tr>
<tr><td colspan="5">15. Supplementary Notes – N/A</td></tr>
<tr><td colspan="5">16. Abstract:

Florida-produced fine aggregates are generally of suitable quality, and deleterious effects associated with organic matter are uncommon. However, naturally occurring organic constituents can affect cement hydration and early-age strength development depending on their concentration, composition, and interaction with cementitious phases. The sands evaluated in this study contained relatively low organic contents, making establishment of a universal organic-content threshold impractical. FDOT currently uses AASHTO T 21 as the primary screening method for potentially deleterious organic impurities and requires AASHTO T 71 testing when screening results indicate concern. This framework should be maintained. AASHTO T 21 provides effective statewide screening, while AASHTO T 71 provides performance-based confirmation. However, AASHTO T 21 is qualitative, and AASHTO T 71 requires extended testing that can delay aggregate acceptance decisions. Neither elemental analysis nor the Modified Walkley-Black method demonstrated sufficient precision, consistency, or correlation with AASHTO T 21 to support statewide acceptance criteria. However, MWB may be used to establish mine-specific organic-carbon baselines, and isothermal calorimetry may be used to establish mine-specific hydration-response baselines. Deviations from these baselines may indicate the need for additional evaluation, including AASHTO T 71 testing. Organic-carbon contents below approximately 0.015% did not measurably affect hydration or compressive strength. Alkaline washing reduced measured organic content and increased pH but did not consistently improve strength. The ASTM C109 hand-tamped consolidation procedure is recommended for AASHTO T 71 mortar cube fabrication. Trace inorganic constituents, including phosphorus, did not produce measurable strength effects.</td></tr>
<tr><td colspan="3">17. Keywords: Silica sand, Fine Aggregate, Organic Impurities, AASHTO T 21, AASHTO T 71, Modified Walkley-Black, Isothermal Conduction Calorimetry, Organic Matter</td><td colspan="2">18. Distribution Statement
No restrictions.</td></tr>
<tr><td>19. Security Classif. (of this report)
Unclassified.</td><td colspan="2">20. Security Classif. (of this page)
Unclassified.</td><td>21. No. of Pages
130</td><td>22. Price</td></tr>
</table>

EXECUTIVE SUMMARY

Background

Overall, the sands used for fine aggregate in Florida are of good quality, and the problems borne from organic matter in sands are uncommon. However, there have been some observances where organic matter in sands has shown the potential to affect the early age strength of portland cement concrete and mortar. Sand or fine aggregate is a primary component of portland cement concrete and mortar, and the quality of sand directly influences the performance of the cementitious system. Because natural sands are sourced from geological deposits, they may contain small amounts of organic matter and other constituents capable of interfering with cement hydration and strength evolution of and mortar at early ages. The relationship between strength and organic matter depends on the type of organic compound present, concentration, and the mechanisms through which it interacts with cement phases. The Florida sands evaluated in this study contained relatively low concentrations of organic matter. When combined with the largely qualitative nature of standardized methods for detecting organic matter, these low concentrations make establishing a reliable threshold for aggregate qualification particularly challenging. Moreover, the presence of organic matter alone does not necessarily indicate deleterious effects on concrete performance.

Currently, the Florida Department of Transportation (FDOT) utilizes AASHTO T 21, Standard Method of Test for Organic Impurities in Fine Aggregates for Concrete, which is a qualitative colorimetric test as a screening tool to identify organic content in fine aggregates. When the test shows a color change that indicates higher organic content, the Department requires follow-up testing using AASHTO T 71, Standard Method of Test for Effect of Organic Impurities in Fine Aggregate on Strength of Mortar, for strength to verify that the added organics are not affecting concrete performance. While this framework provides a basis for aggregate qualification, both tests present limitations. AASHTO T 21 is qualitative and selective, capturing only alkali-soluble organic matter, and has historically produced false positives in some of the fine aggregate mines in the state of Florida mines. The use of the compressive test per AASHTO T 71 is time-intensive, delaying aggregate acceptance, and presents potential sources of variability related to the alkaline washing procedure and mortar cube consolidation method. These limitations motivate the evaluation of alternative and testing approaches for testing including quantitative organic carbon testing determination and accelerated performance-based testing using isothermal conduction calorimetry.

Research Objectives

The primary objectives of this research were to evaluate the mechanisms by which the presence of organic matter in Florida fine aggregates influences concrete strength, assess the temporal variability of organic content in sands from selected Florida mines, investigate the effects of the alkaline washing procedure on sand properties and performance measured by AASHTO T71, evaluate consolidation methods for mortar cube fabrication, and examine the potential influence of inorganic constituents such as phosphorus on strength development

Main Findings

The concentrations of naturally occurring organic matter in the Florida sands evaluated in this study were generally low therefore the research concluded the following:

- Isothermal conduction calorimetry may serve as a supplemental performance-based characterization method for establishing source-specific hydration-response baselines for sands produced from individual mines. Once a baseline and expected range of variability are established, subsequent calorimetry results may be used to identify changes in cement hydration that warrant additional evaluation, including AASHTO T 71 mortar compressive-strength testing. Isothermal conduction calorimetry should not be used as a stand-alone acceptance criterion, as a statewide threshold applicable across independent aggregate sources, or as a direct quantitative replacement for the AASHTO T 21 color scale, unless additional data establishes a defensible performance-based relationship between hydration response and strength performance.
- The modified Walkley–Black method (MWB) may serve as a supplemental quantitative characterization method for establishing source-specific organic-carbon baselines for sands produced from individual mines. Once a baseline and expected range of variability are established, subsequent MWB results may be used to identify measurable increases in organic carbon that warrant additional evaluation. Such a departure should be interpreted as an indication that additional evaluation is warranted, rather than as direct evidence that the sand is deleterious, and confirmation should rely on a performance-based method such as isothermal conduction calorimetry or AASHTO T 71 mortar strength testing. MWB should not be used as a universal quantitative acceptance criterion, as a statewide threshold applicable across independent aggregate sources, or as a direct quantitative replacement for the AASHTO T 21 color scale.
- Results from isothermal conduction calorimetry testing resulted in behavior consistent with that reported for organic matter at low dosages, as samples with the highest measured organic contents exhibited a slight delay in the main silicate hydration peak.
- A single mechanism linking organic matter in Florida fine aggregates to reductions in concrete performance was not established from this evaluation. Organic matter interacts with cement systems through mechanisms that vary with both compound type and concentration.
- Temporal variability of organic carbon in sands from selected Florida mines was conducted over the evaluation period (2022–2024). The organic content of the evaluated sources was found to be consistent over time within the range of available data.
- Alkaline washing increased sand pH and reduced measured organic content, as confirmed by both AASHTO T 21 and modified Walkley-Black measurements.
- The ASTM C109 hand-tamped consolidation method produced mortar cubes with lower normalized variability compared to alternative approaches and is recommended for AASHTO T 71 fabrication.

- Phosphorus was present only in trace amounts and resultant testing did not determine an effect of the T 71 performance or compressive strength. Other inorganic constituents evaluated similarly did not demonstrate a measurable impact on strength development.

Recommendations

Based on the findings of this study, the following recommendations are made:

- AASHTO T 21 should be retained as the primary statewide screening method for identifying potentially deleterious organic impurities in fine aggregate.
- Isothermal conduction calorimetry is recommended as a supplemental performance-based characterization method for establishing source-specific hydration-response baselines for sands produced from individual mines. Subsequent results may be used to identify changes in hydration behavior that warrant additional evaluation, including AASHTO T 71 mortar compressive-strength testing. It should not be used as a stand-alone acceptance criterion or a statewide threshold across independent sources.
- The modified Walkley–Black method is recommended as a supplemental quantitative characterization method for establishing source-specific organic-carbon baselines. Subsequent results may be used to identify measurable increases in organic carbon that warrant additional evaluation. It should not be used as a universal acceptance criterion or a direct replacement for the AASHTO T 21 color scale.
- For fine aggregates with a total organic content in excess of 0.015%, 3-day isothermal calorimetry is recommended as the primary performance-based evaluation tool. Concerns are indicated by a peak magnitude below approximately 90% of control or a peak time delay exceeding approximately 10–15% relative to control. When these thresholds are exceeded, mortar strength testing should be performed. The standard hand-tamped consolidation procedure should be maintained for AASHTO T 71 mortar cube fabrication.

Future Research

Future research should include identifying a range or threshold at which organic carbon begins to exhibit deleterious effects on mortar performance could support the development of acceptance or rejection criteria for aggregates based on organic carbon content alone. This approach has the potential to provide a faster and more cost-effective method for screening harmful organic contents in aggregates, reducing the need for time-intensive AASHTO T 71 28-day mortar cube strength testing.

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1. INTRODUCTION

1.1. Background

Portland cement concrete is composed primarily of cement, water, coarse aggregate, and fine aggregate [1]. Because fine aggregates are naturally sourced materials, they may contain organic matter and other constituents capable of influencing cement hydration and mortar performance. The effect of organic matter on cementitious systems is highly variable and depends on the type of organic compound present, its concentration, and the mechanisms through which it interacts with cement phases and hydration products [2], [3], [4], [5] [6]. Some organic compounds have been associated with retardation of cement hydration and reductions in strength development, while others have shown limited or even beneficial effects under certain conditions [2], [7]. This variability makes aggregate qualification particularly challenging, since the presence of organic matter alone does not necessarily indicate deleterious behavior. As a result, reliable testing methods are needed not only to detect organic contamination, but also to evaluate whether the detected material adversely affects cementitious performance. Ideally, these methods should be rapid, reliable, and capable of distinguishing between organic contents that significantly disrupt hydration and those that do not.

Currently, the Florida Department of Transportation (FDOT) utilizes AASHTO T 21 as a screening tool to identify potentially deleterious organic substances in sands [8]. However, this method is qualitative in nature and does not provide a direct measure of organic content. Additionally, it has historically produced false positives in some Florida mines, where elevated color classifications do not correspond to reductions in strength or performance.

In systems where a sand sample experiences a darker color change per AASHTO T 21 indicating that there is more organic carbon in the system, it must be further evaluated using AASHTO T 71 [9]. This procedure requires the preparation of two batches of mortar cubes: one using the unwashed sand, and the second using the sand after alkaline washing with a 3% sodium hydroxide (NaOH) solution as per AASHTO T 21. FDOT Specification 902-2.2 requires that the seven-day and 28-day compressive strengths mortar cubes from both batches be compared using the unwashed-to-washed strength ratio [10]. Both ratios must exceed 95%, indicating that the unwashed sand does not produce more than a 5% reduction in strength [10] relative to the washed condition. AASHTO T 71 requires compressive-strength testing as 28 days, making it impractical as a routine aggregate-acceptance method because sand production may need to be delayed for up to four weeks while results are pending. Such delays can disrupt mining operations, constrain material availability, and create substantial economic impacts, supporting the need for a rapid screening or accelerated performance-based test.

To address these limitations, FDOT is interested in a rapid, quantitative test capable of determining the effect of organic impurities on strength performance for sand used in concrete. As the organic impurities present in naturally mined sands in Florida are primarily carbon-based, this research evaluated alternatives to AASHTO T 21 for quantifying organic carbon in sand used as fine aggregate in concrete. The study also investigated isothermal conduction calorimetry

as a rapid, performance-based method for assessing the effects of organic impurities on cement hydration.

There are several drawbacks to the AASHTO T 71 testing procedure as it presents two potential sources of variability: the alkaline washing procedure and the consolidation method used for mortar cube fabrication. High alkali content and elevated alkalinity is known to accelerate the hydration of portland cement systems by increasing the dissolution rate of anhydrous cement grains and the precipitation rate of hydration products such as C-S-H [11], [12]. This can lead to faster setting and increased early-age strength [13]. As part of the washing process, if sodium hydroxide (NaOH) used during the washing procedure is not properly and completely removed, residual alkalinity artificially increases the early age strength of the washed samples. Comparative analysis to the unwashed samples indicate that this effect results in a reduced unwashed-to-washed strength ratio, potentially leading to a false indication of deleterious behavior.

Notably, data from the prior phase of this research [3] included two mines, 76349 and 11298, that received a T 21 score of "1" and exhibited total very low carbon contents (below 0.005%) when tested using the modified Walkley-Black method, yet both failed the T 71 mortar cube test. While the mechanism behind these failures was not investigated, the absence of relatively high organic matter in these samples suggests that factors other than organic content likely have contributed to the observed strength reduction, which is consistent with the hypothesis that residual alkalinity from the NaOH washing step could influence T 71 outcomes.

Another potential problem regarding the use of AASHTO T 71 is that it requires the use of water and cement in quantities that will yield a water-to-cement ratio of 0.6 by mass. The consolidation procedure specified in AASHTO T 106, Standard Method of Test for Compressive Strength of Hydraulic Cement Mortar (Using 50-mm or 2-in. Cube Specimens*)*, is based on hand tamping [3]. This method is manual, and operator-dependent, making consistent implementation challenging for relatively inexperienced technicians. As a result, evaluating alternative consolidation methods, such as vibration tables, which are less operator-dependent, is of interest to reduce variability between replicates. The relative size of the cubes, 50-mm (2-in.), any inadequacy in consolidation could lead to entrapped air voids that can significantly affect measured strength. Therefore, identifying the most reliable consolidation practice is necessary toward improving the reproducibility of the test.

Beyond the variability associated with T 71 testing, limitations also exist on the screening side of the evaluation process. In addition to its qualitative nature, AASHTO T 21 may present limitations due to the chemical selectivity of the extracting solution used. The method relies on a sodium hydroxide (NaOH) solution, which is based on the well-established principle that humic substances become soluble under alkaline conditions [14], [15], [16], [17]. Therefore, the extraction is inherently selective toward humic-type organic matter. As a result, other organic compounds that do not respond similarly to alkaline conditions may not be effectively extracted or represented in the test. For example, humin, a common fraction of soil organic matter, is insoluble in both acidic and alkaline conditions and therefore cannot be extracted by NaOH-based methods, potentially leading to an underrepresentation of total organic content [18].

Therefore, the results of the test should be interpreted as indicators of specific types of organic contamination rather than a comprehensive assessment of all organic matter present.

Additionally, one of the major difficulties in evaluating organic matter in natural sands is that both the concentration and composition of the organic material can vary significantly between sources. Because natural sands contain complex mixtures of organic compounds rather than isolated constituents, it becomes difficult to determine whether observed changes in cement hydration or mortar strength are related to the amount of organic matter present, the specific type of organic compound, or interactions between multiple constituents. This variability complicates the establishment of threshold values or acceptance criteria based solely on measured organic content and highlights the need for controlled approaches capable of evaluating the influence of organic matter under more defined conditions.

In addition to organic impurities, the inorganic chemical composition of fine aggregates may also influence mortar performance and the interpretation of standardized test results. Previous studies have reported a slight negative correlation between phosphorus content and AASHTO T 71 mortar strength results, suggesting that phosphorus-bearing constituents may contribute to reduced compressive strength in cementitious systems [3]. Similarly, zinc-containing compounds have been reported to retard cement hydration and alter hydrate formation, leading to delayed setting and reduced early-age strength, with effects strongly dependent on concentration and chemical form [19]. Given these observations, it is also of interest to examine whether specific inorganic elements consistently appear in aggregates from mines that fail AASHTO T 21, particularly those associated with elevated color responses, indicating a potential recurring chemical signature across sources. Therefore, evaluating inorganic constituents alongside organic content may provide a more comprehensive basis for interpreting variability in T 21 and T 71 test outcomes.

Consequently, this study evaluated current screening, characterization, and performance-based methods used for the assessment of deleterious substances in fine aggregates. The testing and analysis included AASHTO T 21, measurement of organic carbon using the modified Walkley-Black testing method, pH testing, Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES), X-ray Fluorescence (XRF), AASHTO T 71 mortar strength testing, and isothermal calorimetry. In addition, controlled sand systems with known additions of organic matter were incorporated to investigate the relationship between organic content, cement hydration behavior, and mortar performance under more controlled conditions. The overall objective was to examine factors influencing current test methods and evaluate whether quantitative organic carbon measurements, hydration-based approaches, or a combination of both could provide a more reliable indication of deleterious behavior in cementitious systems.

1.2. Research Objectives

Quality control of sand and fine aggregate is of paramount importance to ensure the structural adequacy, long-term durability and sustainability of structures owned by FDOT. To ensure the organic components within sand do not exceed minimum threshold values, an evaluation of the materials as well as the test methods themselves will be performed as part of this research

project. It is the goal of the FDOT to find a cheap, quick, and reliable test method for the qualification of organics in fine aggregate and their effect on Portland cement concrete. Currently, the FDOT utilizes AASHTO T 21 and AASHTO T 71 test methods to screen fine aggregate for organic content. This project will hope to answer if a cheaper or faster test method is available as a replacement for either of these current test methods. Primary objectives for this research project include:

- Evaluate and identify a rapid, cost-effective, and reliable screening test that can be used to assess organic impurities in fine aggregates and establish acceptance/rejection criteria as an alternative to 28-day mortar strength testing.
- Perform literature and data review to identify the mechanism by which organic material Florida fine aggregate (sand) impacts concrete strength.
- Determine the temporal variability of organics in sand from various mines in Florida.
- Determine the impacts of alkaline washing of sand to remove organics to improve the cleanliness and performance of sand for use in mortar/concrete.

The secondary objectives of this report are:

- Investigate the consolidation methods for the fabrication of mortar cubes within ASTM C109 and the impacts on the strength variability of mortar.
- Investigate the phosphorus content and the T 71 mortar cube test results between 7 and 28 days to determine the potential impact of phosphorus and other inorganic materials on the strength of concrete.

2. MATERIALS AND METHODS

2.1. Aggregate Sources and Sample Identification

The primary material of interest in this project is fine aggregate from approved FDOT sources. As of the drafting of this report, the University of Florida has acquired samples of approximately 100 pounds of fine aggregate from 5 mines with the help of the FDOT. These sources are outlined in Table 2-1. Mine 05455 provided two samples: one in its natural, unprocessed condition and one after plant washing and processing. These samples are identified by appending the letter N (natural) or P (processed) to the end of the five-digit facility code. Throughout this report, samples in both the as-received condition and after alkaline washing using the AASHTO T 71 procedure are evaluated. When comparisons between these conditions are discussed, the suffix "U" is used to identify unwashed (as-received) samples, and the suffix "W" is used to identify samples subjected to the AASHTO T 71 washing procedure. When no suffix is provided, the sample designation refers to the as-received (unwashed) condition unless otherwise noted.

Table 2-1: Location and Identification of Mine Sands Used in This Study

FDOT Mine ID	Location	District
16564	Davenport, FL	7
16608	Davenport, FL	7
11057	Taveres, FL	5
61377	Chipley, FL	3
05455N	Palmdale, FL	1
05455P	Palmdale, FL	1

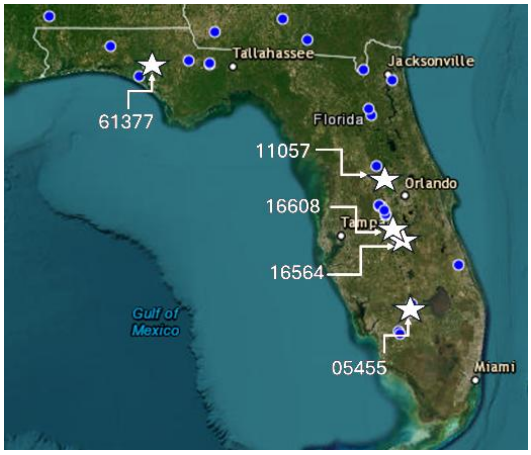

Figure 2-1: Geographic Location of the Mine Sands Evaluated in This Study

For mortar experimental testing done on mine sands, including AASHTO T 71 and isothermal calorimetry, a Type IL (PLC) cement supplied by Argos was used. For mortar experimental testing done on ASTM C778 Standard Graded Sand with controlled organic additions a Type IL (PLC) cement supplied by Ash Grove Cement Company was used. Both cements were used in

as received condition without any additional modification or supplementary cementitious material

Four organic compounds were used in this study to represent different fractions of natural organic matter and add them into cementitious systems: sucrose (crystalline powder form), humic acid (HA) (crystalline powder form), tannic acid (TA) (powder form), and 90% pure fulvic acid (FA) (powder form). All of the acids were obtained from commercial suppliers and used as received without further modification. These materials were incorporated into the experimental program to evaluate their influence on cement hydration and mortar performance under controlled conditions.

Standard graded sand conforming to ASTM C778 was partially replaced by mass with selected organic acids to evaluate the influence of controlled organic additions on cement hydration and mortar performance. Four replacement levels were evaluated for each organic acid type. The replacement levels and corresponding specimen identification codes are summarized in Table 2-2. The control mixture consisted of standard graded sand without organic acid addition and is identified as C-0 throughout this report.

Table 2-2: Nomenclature for Organic-Acid-Dosed Sand Mixtures

Percent Replacement by Weight of Organic Matter	Organic Type		
	Humic	Fulvic	Tannic
0.01%	H-0.01	F-0.01	T-0.01
0.06%	H-0.06	F-0.06	T-0.06
0.15%	H-0.15	F-0.15	T-0.15
0.30%	H-0.3	F-0.3	T-0.3

2.2. Testing Program

Laboratory testing was conducted to evaluate whether organic matter and other constituents present in Florida mine sands affected cement hydration, mortar strength, or aggregate acceptance testing. The testing program included three primary components: screening tests to identify potential organic impurities, material characterization tests to quantify chemical and physical properties of the sands, and performance tests to determine whether the observed constituents produced measurable effects on cementitious behavior. This approach allowed the results of AASHTO T 21 and AASHTO T 71 testing to be interpreted alongside quantitative organic-carbon measurements, pH, elemental composition, gradation, and isothermal conduction calorimetry testing. This constituted a multi-level approach design to evaluate the potential impact of deleterious substances in mine sands on cement hydration and mortar performance..

Screening tests were first conducted using the procedure currently implemented by the FDOT, AASHTO T 21. In addition, the MWB method, which has been proposed as an alternative approach for the quantitative determination of organic matter through carbon content measurement in aggregates, was also evaluated. Carbon content was further measured using an

elemental analyzer (EA), which provides an independent determination of total carbon in the samples. pH testing was also conducted to evaluate conditions that may influence cement hydration or indicate the presence of organic materials.

The AASHTO T 21, MWB, and pH tests were conducted under both unwashed conditions and after washing according to the procedure described in AASHTO T 71. This approach allowed the effectiveness of the washing procedure to be evaluated, as well as its potential influence on measured properties and subsequent mortar strength performance.

Alongside these screening methods, two analytical characterization techniques were used to better understand the elemental composition of the mine sands: ICP-AES and XRF. These analyses were intended to provide insight into the inorganic chemical constituents present in the materials that could potentially influence cement hydration behavior.

Performance testing was used to determine whether the organic matter and other constituents identified during screening and characterization produced measurable effects on cementitious behavior. AASHTO T 71 served as the primary performance-based evaluation, providing a direct comparison of mortar compressive strength produced with unwashed and washed sands. This comparison allowed the influence of organic matter and other removable constituents to be assessed in terms of strength performance rather than screening response alone.

Isothermal conduction calorimetry was also used as an accelerated performance-based characterization method to evaluate cement hydration behavior. Calorimetry provided insight into changes in hydration kinetics, including shifts in the main calcium silicate hydration peak, changes in peak magnitude, and cumulative heat release. These parameters were used to determine whether sands with higher measured organic content produced measurable delays or suppression of cement hydration. However, calorimetry was not treated as a direct replacement for AASHTO T 71 because hydration response alone was not sufficient to predict strength performance across all materials evaluated.

Together, AASHTO T 71 and isothermal conduction calorimetry provided complementary measures of performance. The strength testing established whether the sands produced a measurable reduction in mortar strength, while calorimetry provided insight into the hydration behavior associated with those responses. This combined approach allowed relationships among AASHTO T 21 color response, MWB-measured organic carbon, pH, elemental composition, hydration kinetics, and mortar strength to be evaluated within a common performance-based framework.

A controlled organic-dosing program was also conducted to better isolate the influence of organic matter on cementitious performance. ASTM C778 standard graded sand was used as the reference aggregate and was dosed with selected organic compounds at replacement levels ranging from 0.01% to 0.30% by mass of sand. Use of a controlled sand system minimized the inherent variability associated with natural mine sands and allowed the effects of organic type and concentration to be evaluated more directly. The dosed sand mixtures were evaluated for color using AASHTO T 21, organic carbon using MWB, pH testing, elemental analysis,

isothermal conduction calorimetry, and mortar cube compressive-strength testing. This testing program was designed to examine the relationship among organic content, cement hydration behavior, and mortar strength. The primary objective was to identify the organic-content range at which measurable effects on hydration response or strength performance begin to occur.

2.2.1. AASHTO T 21

AASHTO T 21 served as the primary screening method for identifying potentially deleterious organic impurities in the fine aggregates evaluated in this study. The method is a qualitative colorimetric test in which fine aggregate is immersed in a 3% sodium hydroxide solution for 24 hours. Alkali-soluble organic constituents may dissolve into the solution and produce a color response, which is then compared with the standardized organic plate reference.

A color response darker than organic plate No. 3 indicates that potentially injurious organic impurities may be present and that additional evaluation is required, typically through mortar strength testing in accordance with AASHTO T 71[8, p. 21]. The result should not be interpreted as a measure of total organic content or organic-carbon concentration. The AASHTO T 21 response depends on the solubility, concentration, and color-forming behavior of the organic constituents under alkaline conditions. Consequently, the method provides a screening classification rather than a quantitative measure of organic matter or a direct indication of mortar or concrete performance

For aggregate acceptance, a darker color response than organic plate No. 3 indicates that the sand may contain potentially injurious organic impurities and that additional evaluation is required, typically through mortar strength testing in accordance with AASHTO T 71. However, AASHTO T 21 does not quantify total organic content, nor does it identify the type of organic compound present. The test response depends on the concentration, solubility, and color-forming behavior of the organic constituents under alkaline conditions. As a result, the method is best interpreted as an initial screening tool rather than a direct measure of organic-carbon content or concrete performance.

This study evaluated AASHTO T 21 results in combination with MWB organic-carbon measurements, pH, elemental analysis, isothermal conduction calorimetry, and mortar compressive strength. This combined evaluation allowed the color response to be compared with quantitative chemical measurements and performance-based indicators of hydration behavior and strength development.

2.2.2. Mortar Strength Testing

2.2.2.1. Natural Fine Aggregates

Mortar strength testing was conducted in accordance with AASHTO T 71 to determine whether organic impurities or other removable constituents in the sands produced from Florida mines experience a measurable reduction in compressive strength. Each natural fine aggregate was evaluated in both the unwashed condition and after washing in accordance with the AASHTO T 71 procedure. The same mortar proportions were used for both conditions to provide a direct

comparison between the unwashed and washed sands. Mortar mixing and cube fabrication were performed in accordance with AASHTO T 106 using 50-mm cube specimens. Mix proportions for the nine-cube batches were determined in accordance with AASHTO T 71 and are summarized in Table 2-3. Mortar flow was determined immediately after mixing using the flow table specified in AASHTO M 152/M 152M and reported as the percent increase in spread diameter. Cube specimens were consolidated using the standard hand-tamping procedure, demolded after 24 hours, and cured in lime-saturated water until compressive-strength testing at 3, 7, and 28 days.

Table 2-3: Mix Proportions and Achieved Flow for Mortar Mixtures Prepared According to AASHTO T 71

Mine #	Unwashed Sand (g)	IL Portland Cement (g)	Water (g)	Flow%
16564	2991.6	900	540	107.8
16608	3117.2	900	540	111.5
11057	3293.8	900	540	106
61377	3037.7	900	540	113.7
05455N	3047	900	540	106.8
05455P	3245.9	900	540	105.3

2.2.2.2. Organic Acid Dosed Fine Aggregates

The organic-acid-dosed sand experiment was conducted to isolate the influence of organic matter type and concentration on mortar behavior under controlled aggregate conditions. ASTM C778 standard graded sand was used as the reference aggregate to minimize the variability associated with naturally mined sands and to provide a consistent baseline material. Organic matter was introduced by partial mass replacement of the sand using three selected organic acids: humic acid and fulvic acid, representing humic substances, and tannic acid, representing a non-humic organic compound.

The dosed mixtures were prepared using the same mixing, consolidation, and curing procedures used for the natural fine aggregate testing. Preliminary batching indicated that the cement and water quantities specified for a six-cube batch in AASHTO T 71, when combined with the ASTM C778 standard graded sand quantity specified for a nine-cube batch in AASHTO T 106, produced a nine-cube batch with mortar flow within the target range of 110 ± 5%. To maintain consistency among mixtures, all organic-acid-dosed batches were prepared using 600 g of cement and 360 g of water, with organic matter content serving as the controlled variable.

Organic acids were incorporated at replacement levels of 0.01%, 0.06%, 0.15%, and 0.30% by mass of sand. The corresponding sand replacement masses and measured mortar flow values are summarized in Table 2-4. The controlled dosing program allowed the effects of organic compound type and dosage to be evaluated independently of the mineralogical, gradational, and chemical variability present in naturally mined sands.

Table 2-4: Sand Replacement Masses and Mortar Flow Values for Organic-Acid-Dosed Mixtures

Organic Matter Replacement	Sand (g)	Organic Matter (g)	Humic Acid Flow (%)	Fulvic Acid Flow (%)	Tannic Acid Flow (%)
0.00%*	n/a	0	105.00	105.00	105.00
0.01%	2034.8	0.20	118.44	116.54	111.5
0.06%	2033.8	1.22	119.84	123.9	116.5
0.15%	2032.0	3.05	**	**	118.7
0.30%	2029.0	6.11	**	**	119

*Control Sample (C-0)

** Exceeded the measurable range of the standard flow table procedure

2.2.3. Modified Walkley-Black Method

The MWB method was used as a quantitative characterization method for measuring oxidizable organic carbon in the fine aggregate samples. The procedure used in this study was based on Association of Fertilizer and Phosphate Chemists Procedure No. 17, Organic Matter-C. The method relies on wet chemical oxidation, in which organic carbon present in the sample is oxidized using potassium dichromate under acidic conditions.

This research investigated the use of MWB potential as a potential supplement for the measurement of organic-carbon content rather than as a direct replacement for AASHTO T 21. Unlike AASHTO T 21, which provides a qualitative color response associated with alkali-soluble organic impurities, the MWB provides a quantitative measurement of oxidizable organic carbon. However, the method does not identify the type of organic compound present and does not directly indicate whether the measured organic carbon will adversely affect hydration or strength. Accordingly, MWB results were interpreted in conjunction with AASHTO T 21 color ratings, pH, elemental analysis, isothermal conduction calorimetry, and mortar compressive-strength results.

2.2.4. Elemental Analyzer

For this study, elemental analysis was interpreted as a measure of total carbon rather than organic carbon. This distinction is important because total carbon may include both organic carbon and inorganic carbon associated with carbonate minerals, shell fragments, carbonate fines, or carbonate coatings on aggregate particles. Therefore, results obtained via EA were not treated as a direct equivalent to organic carbon using MWB, which measures oxidizable organic carbon. Instead, elemental analysis was used as a supplemental characterization method to evaluate general carbon trends and to assess whether total carbon measurements were consistent with organic carbon results, AASHTO T 21 color response, pH, calorimetry, and mortar strength performance. were weighed and encapsulated in tin capsules prior to analysis. Elemental composition was determined using a Carlo Erba NA1500 CNHS elemental analyzer equipped with a 50-position automated Zero Blank sample carousel. Samples underwent flash combustion

at 1020 °C in a quartz column containing chromium oxide and silvered cobaltous/cobaltic oxide under an oxygen-rich atmosphere. The resulting combustion gases were transported by a helium carrier stream through a reduction column maintained at 650 °C and packed with reduced elemental copper to remove excess oxygen.

2.2.5. Elemental Analysis

Two complementary analytical techniques were employed to quantify the elemental composition of the sand samples. X-ray fluorescence was used to determine major elemental oxides in solid samples, while Inductively Coupled Plasma–Atomic Emission Spectrometry was used to quantify trace elements at lower concentrations. XRF and ICP-AES are complementary in nature, as XRF provides robust and highly repeatable measurements of major elements in silicate-based materials, whereas ICP-AES offers higher sensitivity for detecting trace-level constituents that may fall below XRF detection limits. This combined analytical approach enables comprehensive characterization of both major and trace inorganic constituents potentially influencing cement hydration and mortar performance. ICP-AES testing was done following EPA Method 200.7 [20].

For XRF analysis, samples were first weighed into platinum crucibles and heated at 950°C for 1 hour to determine loss on ignition (LOI). Subsequently, 1.3 g of ignited sample was mixed with 6.5 g of flux (66% lithium tetraborate, 34% lithium metaborate, and 0.5% lithium bromide) and fused in a high-temperature fusion machine to produce a homogeneous glass bead. The fused beads were analyzed using a Thermo ARL 9900 X-ray fluorescence spectrometer. Calibration curves were selected depending on material type: NIST-traceable standards for cement-related materials, in-house raw material standards for feed materials, and the manufacturer's Uniquant calibration for unknown samples.

2.2.6. pH Testing

pH testing was conducted in accordance with the Florida Method of Test for pH of Soil and Water, FM 5-505 [21]. Measurements were performed on each fine aggregate in both the unwashed condition and after washing in accordance with the AASHTO T 71 procedure. Testing both conditions allowed changes in the sand-water system caused by alkaline washing to be evaluated. The pH measurements were used as a supplemental chemical characterization method. Organic-bearing sands may exhibit lower pH due to the presence of organic acids or acidic functional groups associated with humic substances. However, pH is not a direct measure of organic content and may also be influenced by soluble salts, carbonate buffering, mineralogy, fines content, and other constituents present in the aggregate. Accordingly, pH results were interpreted in conjunction with AASHTO T 21 color ratings organic carbon via MWB, total carbon via EA, isothermal conduction calorimetry, and mortar compressive-strength results.

2.2.7. Isothermal Calorimetry

Isothermal conduction calorimetry was used to evaluate the influence of naturally mined sands and controlled organic additions on the hydration behavior of mortar mixtures. The method measures the rate of heat evolution from hydrating cementitious systems maintained at a constant

temperature. Because cement hydration is exothermic, changes in heat-flow response provide an indication of changes in hydration kinetics, including acceleration, retardation, suppression of hydration reactions, and changes in cumulative heat release.

The testing approach was generally consistent with the principles of ASTM C1679 and ASTM C1702. ASTM C1679 provides guidance for measuring hydration kinetics of hydraulic cementitious mixtures using isothermal calorimetry, while ASTM C1702 provides procedures for determining heat of hydration using isothermal conduction calorimetry. In this study, the calorimetry specimens were prepared as mortar mixtures containing the fine aggregate being evaluated, rather than as cement paste mixtures. This approach allowed the measured heat-flow response to reflect the interaction between the cementitious system and the sand, including any effects associated with organic matter, soluble constituents, fines, or aggregate surface characteristics.

Calorimetry was used primarily as a comparative performance-based characterization method rather than as an acceptance test. The response of each mortar mixture was interpreted relative to a control or source-specific baseline mixture prepared using the same cementitious materials, fine aggregate condition, and mixture proportions. The primary parameters extracted from the heat-flow curves included the time and magnitude of the main calcium silicate hydration peak, the time and magnitude of the secondary aluminate-related peak, and cumulative heat release at selected ages. Particular emphasis was placed on shifts in the main calcium silicate peak time because delayed peak occurrence was the most consistent calorimetric indicator of organic-related hydration effects. Cumulative heat release was also evaluated; however, it was not treated as a stand-alone predictor of strength performance because similar cumulative heat values did not always correspond to similar mortar strengths.

A draft Florida Standard Method of Test was developed as part of this study to provide a rapid, performance-based procedure for evaluating fine aggregates containing organic impurities using isothermal conduction calorimetry in Appendix A. The draft method, titled “Draft Florida Standard Test Method for Qualification of Fine Aggregates Containing Organic Impurities Using Isothermal Conduction Calorimetry”, is adapted from the measurement concepts of ASTM C1702/C1702M and modified for mortar systems containing the fine aggregate being evaluated. The method is intended to provide a supplemental approach for identifying changes in cement hydration response associated with organic matter in fine aggregate and to support decisions regarding when additional performance testing, such as AASHTO T 71 mortar compressive-strength testing, may be warranted.

2.2.7.1. Mined Sands

For mine sands hydration kinetics and heat of hydration of the mortar mixtures were evaluated using an eight-channel TAM Air isothermal calorimeter (TA Instruments) operated at a constant temperature of 23 °C [22]. Testing was conducted following the general procedure outlined in ASTM C1702 for externally mixed samples [23].

Cement, sand, and water were combined directly in glass vials at a cement–sand–water ratio of 1:1:0.5 and homogenized using a vortex mixer at 2500 rpm for 5 s. Immediately after mixing, the fresh paste was transferred into glass ampoules for testing. Each ampoule was filled to the target mass with a tolerance of ±0.002 g, hermetically sealed, and placed in the calorimeter alongside a corresponding reference ampoule. Heat flow and cumulative heat evolution were recorded continuously throughout the test duration. The resulting data were normalized by cement mass and reported as heat flow (mW/g) and cumulative heat (J/g). All mixtures were tested in duplicate to ensure repeatability.

To ensure accurate heat measurements, based on the proportions, the sample heat capacity was matched to that of the Duratherm reference fluid by accounting for the specific heat capacities of all constituents. The total sample mass was then calculated to satisfy this heat capacity balance, which in turn determined the masses of each constituent placed in the vial.

2.2.7.2. Dosed Sands Experiment

For the controlled organic matter experiments, calorimetry specimens were prepared from mortar batches produced using a Hobart mixer, following AASHTO T 106 procedure, rather than by direct mixing within individual sample vials. This approach was adopted because the target organic dosages were extremely low and could result in increased variability when preparing individual calorimetry specimens and mixing in the vials. In addition, some humic acid exhibited limited solubility in water, making it difficult to ensure uniform distribution. Preparing larger mortar batches allowed the organic additions to be incorporated more uniformly and ensured consistency between calorimetry specimens and the corresponding mortar cube mixtures used for strength testing.

Following mixing, fresh mortar was transferred to a sealed container and transported to the calorimetry preparation area. Representative portions of the mortar were then weighed into glass ampoules. Similar to the mine sand procedure, the target sample mass was determined through heat-capacity balancing calculations that considered the masses and specific heat capacities of all components, including cement, sand, water, organic matter, the glass ampoule, and the Duratherm reference fluid. Sample masses were adjusted as necessary to ensure that the overall heat capacity of the sample matched that of the reference system. A tolerance of ±0.002 g from the target mass was permitted during ampoule filling.

After loading, ampoules were immediately hermetically sealed using a crimping tool and placed in the calorimeter together with the corresponding reference ampoules. The exact insertion time was recorded for each specimen to allow correction of the effective reaction start time during data processing.

Testing was conducted for seven days. Following completion of the test, heat flow and cumulative heat data were exported and processed. The reaction start time was adjusted based on the recorded mixing and insertion times. Heat flow and cumulative heat were calculated and normalized by the mass of cement present in each specimen, which was determined from the

total sample mass and the known mortar mixture proportions. Results were reported as heat flow (mW/g cement) and cumulative heat release (J/g cement).

3. ORGANIC MATERIAL IMPACTS ON MORTAR STRENGTH

The influence of organic matter on cement hydration and mortar performance is not fully understood, and this uncertainty stems from three compounding factors: the diversity of organic compound types, the variability in how each type interacts with cementitious phases, and the difficulty of detecting and characterizing them within aggregate materials. Together, these factors make it challenging to establish universal screening criteria or predict performance based on organic content alone. Understanding these mechanisms can help clarify what chemical and physical changes are most relevant to observe when evaluating the effect of organic matter on cement systems. While not all types of organic matter have been studied in the context of cement, some compounds have been evaluated, and efforts have been made to explain their mechanisms and effects on hydration. The following section summarizes the main mechanisms documented in the literature, with the goal of identifying trends in how certain organics affect cement reactions and what that means for performance evaluation.

.Organic matter present in soils and natural aggregates consists of the fraction derived from the decomposition and transformation of plant and microbial remains [24]. This fraction is highly variable in both composition and structure, and is therefore commonly divided into two broad categories: humic substances (HS) and non-humic substances (non-HS) [25]. Humic substances are characterized by poorly defined chemical structures and heterogeneous compositions, and are generally understood to have undergone significant transformation from their original biological sources [17], [24]. They represent the most abundant fraction of natural organic matter, accounting for as much as 85–90% of the total organic content, and are typically dark in color [26]. Humic substances are further classified based on their solubility behavior into humic acid, which is soluble in alkaline conditions but precipitates at pH < 2; fulvic acid, which is soluble across all pH ranges; and humin, which remains insoluble [17], [24]. In contrast, non-humic substances consist of compounds with recognizable and more defined chemical structures. They represent a smaller fraction of the total organic matter, typically on the order of 10–15%, but are widely distributed across many distinct compound types [26]. These substances are classified according to their chemical nature and include groups such as polysaccharides, polypeptides, lipids, lignins, tannins, and resins [26]. This distinction, between structurally ambiguous but dominant humic substances and structurally defined yet highly diverse non-humic compounds, highlights the inherent complexity of organic matter and the difficulty in characterizing its composition and predicting its behavior.

The effect of these compounds on cement is not uniform. The most commonly reported effect at low dosages is retardation of cement hydration [2], [3], [4], [5] [6] frequently accompanied by a reduction in strength [4], [5], [27]. However, some organic materials have been shown to have negligible effects or even to improve certain aspects of cementitious performance under specific conditions [4], [6], [27] suggesting that the presence of organic matter in an aggregate does not, by itself, indicate harmful behavior. What has been consistently identified in the literature is that the functional groups present in organic compounds play a governing role in their interaction with cementitious systems [2], [7]. A functional group is a characteristic group of atoms or bonds that possesses predictable chemical behavior [28]. Different functional groups have been shown

to influence cementitious systems through different mechanisms; for example, some can bind or chelate metal ions, whereas others can modify the pore solution pH, both of which can directly affect cement hydration [2], [7]. As a result, the type, concentration, and functional group composition of the organic compound ultimately determine its effect, which is what makes aggregate screening so difficult in practice.

The complexity described above also creates challenges for existing screening approaches. As discussed previously, AASHTO T-21 presents two important limitations: it is selective because it primarily captures alkali-soluble organic compounds, leaving other classes of organics potentially undetected, and it is qualitative because the resulting color response does not provide a direct measure of organic content or indicate the severity of its effect on cement hydration. When combined with the broad diversity of organic matter and the variability of its interaction mechanisms, these limitations make predicting cement performance from screening results alone particularly difficult. A more informative approach lies in understanding the specific mechanisms by which organic compounds interact with cement phases, particularly those governing C-S-H formation, which is the primary contributor to strength development. Examining these mechanisms not only clarifies why certain organics are deleterious while others are not, but also helps identify the characteristics most relevant for a performance-based evaluation approach.

Among the compounds studied in cement systems, the mechanisms associated with sucrose have been among the most extensively investigated and are relatively well established. Therefore, sucrose is discussed first as a reference case because it introduces several concepts that are relevant to understanding the behavior of other organic compounds in cement systems. Sucrose has been established as a well-documented retardant of cement hydration [2], [29], [30], [31], [32]. Retardation occurs through two simultaneous processes. From the moment sugar contacts cement, it chelates to the surfaces of unreacted cement grains through its hydroxyl functional groups [29], interacting with calcium-bearing cement phases at the grain surface. This interaction increases the dissolution of calcium ions from the cement grains into the pore solution [30], [31], [32], leading to elevated calcium concentrations in solution. Simultaneously, as early C-S-H and CH begin to form, sugar adsorbs onto their surfaces, poisoning these sites and preventing dissolved ions from attaching and precipitating. Sugar therefore interacts with both unreacted cement grains and forming hydration products at the same time, making retardation highly effective. As a result, elevated concentrations of calcium ions remain in the pore solution because the poisoned hydration product surfaces cannot act as nucleation sites [2]. Instead, ions nucleate independently throughout the pore solution. This distinction is important because independent nucleation requires substantially more energy than nucleation onto existing surfaces, causing hydration to slow dramatically rather than simply redirecting [2].

The extent of retardation depends on the balance between the available sugar concentration and the formation of new nucleation sites. When sufficient sugar is present, adsorption onto cement grain surfaces and early hydration products can inhibit normal precipitation and delay hydration. As hydration products continue to form, however, the number of available nucleation sites eventually exceeds the amount of sugar available to poison them. Once this threshold is exceeded, clean nucleation sites become available, and hydration can proceed rapidly. Because

ions accumulated in the pore solution during the retardation period, renewed hydration may progress quickly and can surpass the degree of hydration observed in control pastes [2]. Once the retardation barrier is overcome, new C-S-H grows preferentially onto clean unpoisoned sites and it has been suggested that sugar is eventually incorporated into the hydration products [2], however, there is not sufficient evidence to conclude that this produces fundamentally different or lower-quality C-S-H. Because the strongest retardation effects occur at low degrees of hydration, any early hydration product formed on poisoned surfaces is likely limited in volume relative to the larger amount of C-S-H that develops after normal hydration resumes.

While retardation represents an initial penalty, the overall effect of sucrose on cement microstructure appears more nuanced. At higher degrees of hydration, sugar-containing pastes exhibit a refined pore structure, characterized by fewer large capillary pores and a greater proportion of nanoscale gel pores, which collectively correspond to a reduction in total porosity [2]. This refinement occurs because during the retardation period, ions nucleated independently at many distributed sites throughout the paste rather than concentrating near cement particle surfaces. When hydration resumed, C–S–H formed across this distributed network, which influences the type of C–S–H and the arrangement of the hydration products. C–S–H can be divided into two types: low-density and high-density C–S–H [33]. Low-density C–S–H is characterized by a more open gel structure, higher internal porosity, lower stiffness, and greater susceptibility to chemical degradation compared to high-density C–S–H [34]. Sucrose, due to the distributed nucleation sites, creates a greater proportion of low-density C–S–H. While this may appear detrimental, the resulting products are packed more uniformly, reducing overall porosity [2]. The result is an overall finer and more connected pore network. Since larger capillary and macropores are known to reduce strength and stiffness, whereas nanoscale gel pores have a negligible adverse effect, a shift toward finer pores represents a potentially beneficial microstructural outcome despite the initial retardation penalty [35].

Building on the concepts introduced through sucrose, tannic acid represents another non-HS that has also been reported to retard cement hydration, although its effects on long-term strength development are mixed, with studies showing both reductions and improvements [4], [6], [36]. Similar to sucrose, tannic acid contains hydroxyl functional groups, which have been associated with retardation mechanisms in cement systems. In addition, tannic acid has been shown to bind metal ions in aqueous systems and is widely considered to act as a chelating agent. Therefore, similar interactions with metal ions in cement pore solutions can be expected [37].

Studies have shown via FTIR testing that TA, similar to the behavior described for sucrose, binds to both cement phases and hydration products through hydrogen bonding interactions [4], [7]. Consistent with the mechanisms previously discussed, the presence of TA has also been associated with reduced porosity and refined pore structures [4], [7]. This interpretation is further supported by nanoindentation and modeling results, which show an increased fraction of low-density C-S-H in the presence of TA, accompanied by higher packing density and more homogeneous elastic properties. These findings confirm that, although TA promotes the formation of low-density C-S-H, the resulting hydration products are more uniformly distributed and structurally refined, leading to a denser microstructure and improved mechanical

performance [4], [7]. These microstructural changes translate to increased compressive strength due to improved packing density and reduced porosity [4].

While sucrose and tannic acid provide useful reference cases for understanding individual interaction mechanisms in cement systems, the previous classification of organic matter highlighted that humic substances represent the most abundant fraction of natural organic matter in soils and aggregates. Within this fraction, humic acid and fulvic acid are distinguished based on their solubility behavior, which directly governs their availability and reactivity in high-pH cement pore solutions. HA differs from the previously discussed compounds in both functional group composition and solubility behavior, it presents carboxyl (–COOH) and phenolic (–OH) groups and is only soluble under alkaline conditions, which is particularly relevant given the high pH environment of cement pore solutions.

Despite these structural differences, HA shares with the previously discussed compounds a capacity for calcium complexation that disrupts cement hydration. Similar to tannic acid, HA has well-documented heavy metal binding capabilities in environmental systems [38], [39], and more specifically, has been shown to have a strong chemical affinity for calcium [40]. Because of this characteristic, HA reacts with calcium ions released during cement hydration to form insoluble calcium humate [40], [41], which adsorbs onto the surfaces of unreacted cement grains, physically blocking further hydration[5], [7]. This retention of calcium ions in an insoluble form reduces their availability to form hydration products and retards strength gain [5], [7], [40] [41]. Unlike the behavior described for sucrose and tannic acid, reports on HA interaction focus primarily on this coating of unreacted cement grain surfaces and calcium sequestration in the pore solution, with less documentation of direct adsorption onto already-formed hydration products. Notably, no recovery mechanism has been described for HA, the conditions under which hydration may proceed past this inhibition remain unclear.

An additional effect reported for HA, and less documented for the previously discussed compounds, is its influence on pore solution pH. HA has been shown to decrease the pH of the pore solution in cement systems [5], [27], altering the highly alkaline environment that governs cement hydration reactions. This represents a compounding effect beyond calcium sequestration alone, since elevated pH promotes the dissolution of calcium silicate phases and the formation of hydration products [12], a reduction in alkalinity can suppress these processes and limit hydration.

The combined result of these mechanisms is a reduction in strength development [5], [7], [27], [40]. A threshold behavior has also been reported, where strength declines progressively up to a certain organic content, beyond which further increases no longer produce additional strength reduction [5], [7]. The mechanism behind this plateau remains unexplained in literature, representing an additional aspect of HA behavior in cement systems that is not yet fully understood.

Fulvic acid represents the second major fraction of humic substances and, as previously noted, differs from humic acid in its solubility behavior, remaining soluble across all pH conditions, including the highly alkaline cement pore solution [7], [17], [24], [41]. This continuous

solubility is particularly relevant in cement systems, as it ensures FA remains available in solution throughout the hydration process, from initial mixing to later-age reactions. Structurally, FA shares carboxyl (–COOH) and phenolic (–OH) functional groups with humic acid, enabling similar interactions with calcium ions and cement phases. The mechanisms previously described for humic acid, including calcium complexation and pore solution pH reduction, have also been reported for FA [7], [41]. In addition, a threshold behavior similar to that observed for humic acid has been reported, where reductions in strength occur up to a limiting content, beyond which further increases in fulvic acid concentration produce minimal additional effect [7].

In addition to these shared mechanisms, fulvic acid has been reported to directly affect already-formed hydration products. Studies indicate that FA can decompose calcium- and aluminum-containing hydration phases, including C-S-H and related gel structures, by dissolving calcium and aluminum ions back into the pore solution [7]. Evidence of this effect is reflected in the reported decrease in hydration product content with increasing FA concentration, as well as SEM observations of a more porous and discontinuous microstructure [7]. This decomposition capacity, combined with the inhibition of new hydration product formation, results in a more severe disruption of microstructural development compared to HA, which is consistent with the significantly greater reductions in strength reported for FA at similar concentrations [7].

The mechanisms reviewed here illustrate that organic matter does not interact with cement systems in a uniform way. Sucrose and tannic acid primarily act through retardation and nucleation interference, humic acid through calcium sequestration, surface blocking, and pH reduction, and fulvic acid through all of these mechanisms combined with the capacity to decompose already-formed hydration products. Despite these differences, a common thread emerges: the critical question in each case is not whether organic matter is present, but whether C-S-H is forming properly and whether hydration is proceeding as expected. This is precisely what a color-based or even quantitative screening test cannot capture, as the same total organic content can produce vastly different effects depending on which compounds are present and at what concentration. Isothermal calorimetry, by directly measuring the rate and progress of cement hydration, offers a performance-based alternative that is sensitive to these interactions regardless of organic type, making it a more reliable indicator of whether a given aggregate will affect cementitious performance in practice.

4. RESULTS AND DISCUSSION

4.1. Screening and Characterization of Natural Fine Aggregates

4.1.1. Particle Size Analysis

Sieve analysis was performed on each mine in accordance with AASHTO T 27 Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates [42] and the resulting gradations were compared with the limits specified in FDOT's Standard Specification 902 for Silica Sand [10]. The results are presented in Table 4-1.

The evaluated materials exhibited gradations consistent with fine aggregates commonly produced from Florida sand deposits, including relatively high percentages passing the No. 30, No. 50, and No. 100 sieves. Fineness modulus values ranged from 1.86 to 2.56, indicating meaningful variation in particle-size distribution among the sources. Mines 05455N and 05455P represented the finer materials in the dataset, whereas mines 16564 and 16608 exhibited comparatively coarser gradations. These differences were considered during interpretation of the mortar strength and calorimetry results because gradation, fines content, surface area, and particle packing can influence measured performance independently of organic content.

Table 4-1: Gradation Analysis Results (Percent Passing) for All Mines

Sieve Designation	Lower Passing Spec Limit (%)	Upper Passing Spec Limit (%)	16564 Passing (%)	16608 Passing (%)	11057 Passing (%)	61337 Passing (%)	05455N Passing (%)	05455P Passing (%)
3/8 in.	100	100	100	100	100	100	100	100
No. 4	95	100	100	100	100	100	100	100
No. 8	85	100	99.7	99.9	99.8	99.2	99.7	99.6
No. 16	65	97	92.2	92.5	94.1	86.9	94.9	94
No. 30	25	70	41.5	53.4	62.5	54.8	72.6	67.9
No. 50	5	35	8.2	11.7	24.6	29.4	37.7	32.1
No. 100	0	7	2.5	2.3	4.5	3.7	9	8.5
No. 200	0	4	0.2	0.1	0.1	0.1	0.4	0.4
Pan	n/a	n/a	0	0	0	0	0	0
Fineness Modulus	n/a	n/a	2.56	2.4	2.15	2.26	1.86	1.98

4.1.2. AASHTO T 21 Screening Results

T 21 was conducted on the mines in its as-received condition and after washing using a 3% sodium hydroxide (NaOH) solution following the procedure outlined in AASHTO T 71. Figure 4-1 shows the results obtained with the sands in their as-received condition, while Figure 4-2 shows the results after washing with NaOH Table 4-2 presents these results in comparison to the organic plate number value.

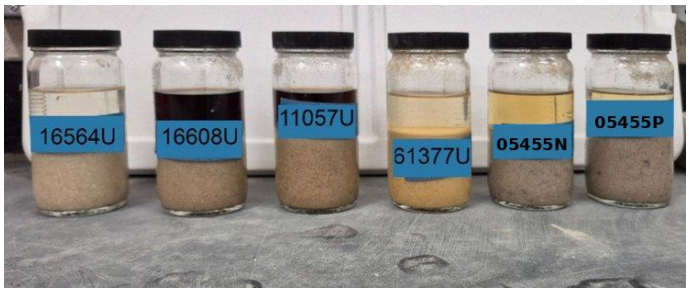

Figure 4-1: AASHTO T 21 Color Test Results for Mine Sands in As-Received Condition

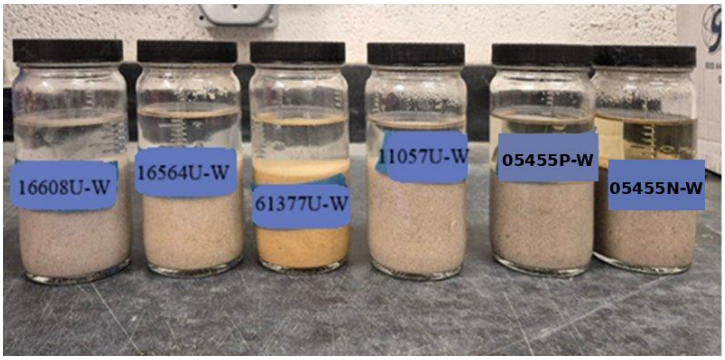

Figure 4-2: AASHTO T 21 Color Test Results After Washing According to the AASHTO T 71 Procedure

The T 21 test conducted on the sand in their as-received condition indicated that two out of the six samples (Mines 16608 and 11057) produced color values greater than 3 when compared with the Organic Plate Number Table 4-2. In accordance with AASHTO T 21, these samples are considered to potentially contain injurious organic compounds and therefore require further evaluation prior to approval. Subsequent T 21 testing was conducted following the washing procedure outlined in AASHTO T 71 and re-evaluated. After washing, all samples produced color values of 1, indicating, that the washed materials are free of deleterious substances. Larger batches of each sand were subsequently washed using the same procedure and used in all subsequent tests and comparisons presented in this report.

Table 4-2: Color Test Results per AASHTO T 21 – Unwashed and Washed

MINE ID	Organic Plate Number	
	Unwashed	Washed
16564	1	1
16608	5*	1
11057	5*	1
61377	1	1
05455N	2	1
05455P	1	1

Additional testing was conducted on sand from mines 16608 and 11057, both of which received an AASHTO T 21 color rating of 5 in the as-received condition. The samples were subsequently separated by particle size, and the No. 100 sieve fraction was isolated for further evaluation using AASHTO T 21 and isothermal conduction calorimetry The results shown in Figure 4-3 and Table 4-3 show that the isolated No. 100 fractions from both mines also received a color rating of 5. The corresponding bulk samples produced the same rating, indicating that organic matter concentrated within the finer fraction may have contributed substantially to the overall AASHTO T 21 response of these materials.

Table 4-3: AASHTO T 21 Color Test Results for No.100 Sieve Fraction Results.

MINE ID	Organic Plate Number no. 100 Sieve
16608	5*
11057	5*

* Fails AASHTO T 21

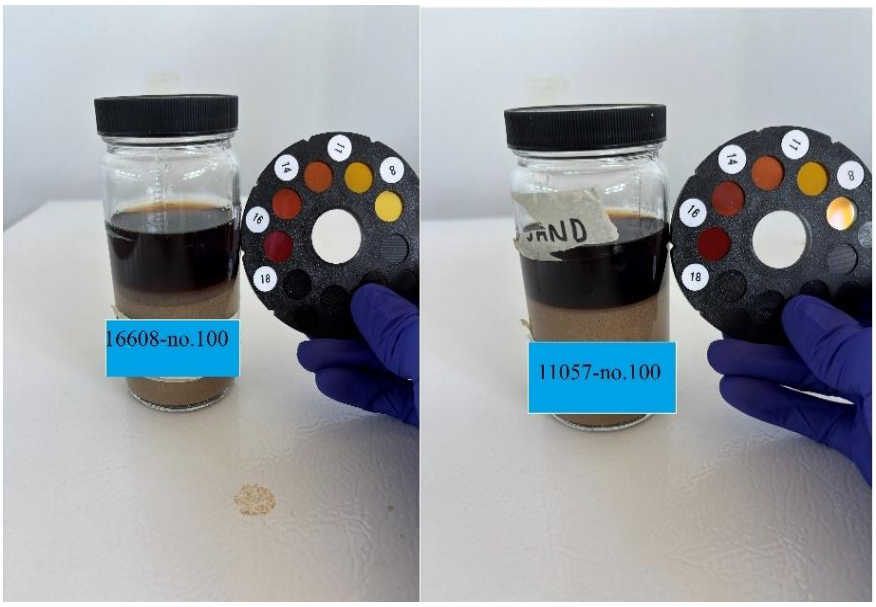

Figure 4-3: AASHTO T 21 Test Conducted on No.100 Sieve Fraction

4.1.3. Relationship Between AASHTO T 21 and Modified Walkley–Black Results

The modified Walkley–Black test was performed on each sand in both the unwashed condition and after washing in accordance with the AASHTO T 71 procedure. The results are presented in Table 4-4. The mines with an AASHTO T 21 color rating of 5 were generally among those with the highest measured organic content. Mine 11057, which did not meet the AASHTO T 71 strength criterion at 28 days, also exhibited the highest measured organic content. Although this observation suggests that elevated organic-carbon content may be associated with an increased likelihood of deleterious strength behavior, the available data do not support establishment of a

universal organic threshold. The response appears to be source-specific and may also be influenced by physical aggregate characteristics, including gradation, fines content, and particle packing.

Table 4-4: Organic Carbon Measured by the Modified Walkley–Black Method for Unwashed and Washed Samples

MINE ID	Organic carbon (%, avg)	
	Unwashed	Washed
16564	0.0011	0.0029
16608	0.0134	0.0014
11057	0.017	0.0059
61377	0.0067	0.0045
05455N	0.0145	0.0136
05455P	0.0103	0.0097

The relationship between MWB-measured organic carbon and AASHTO T 21 color ratings is presented in Figure 4-4 using the MWB results in Table 4-4 and the AASHTO T 21 A general positive association was observed, with higher organic Carbon content was measured for sand with higher T 21 color ratings. However, the relationship was not sufficiently consistent to support direct conversion between the two methods. The Pearson coefficient was ($r = 0.653$), with an ($R^2 = 0.426$), indicating that MWB-measured Organic Carbon explained only a portion of the variability in T 21 response. This is consistent with the qualitative nature of AASHTO T 21, which is influenced by both the concentration and type of organic matter present. Therefore, MWB should be interpreted as a supplemental quantitative characterization method rather than as a direct quantitative replacement for the AASHTO T 21 color scale.

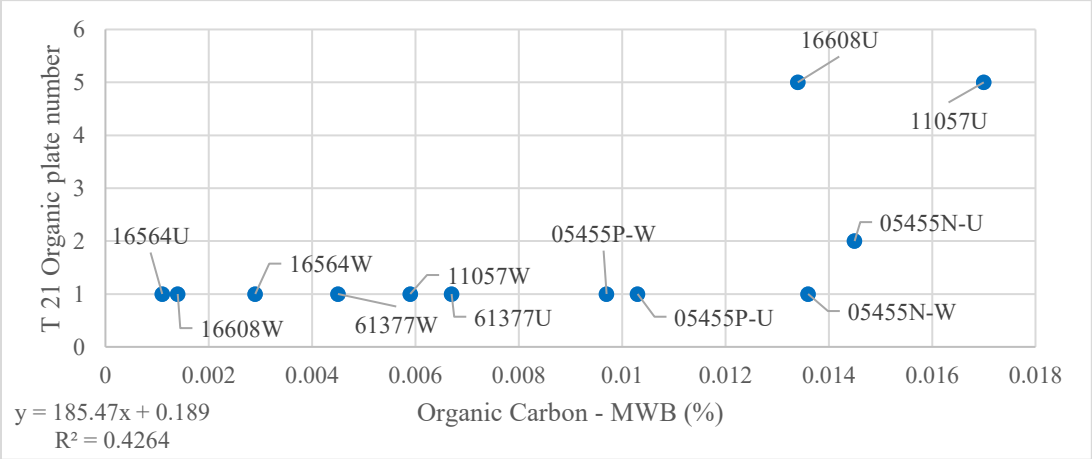

Figure 4-4: Organic Carbon vs. AASHTO T 21 Color Rating

The relationship between organic carbon measured with the modified Walkley–Black method and AASHTO T 21 color rating is presented in Figure 4-4. The data do not support a uniform linear relationship; instead, they indicate an apparent threshold-sensitive response. Nearly all samples containing less than approximately 0.012% organic carbon received an AASHTO T 21

plate number of 1. Above this concentration, the color response increased sharply for several sources, most notably mines 16608 and 11057, both of which received a plate number of 5.

The transition near 0.012% was not universal. Mine 05455N contained organic carbon above this level but produced a substantially lower plate number, demonstrating that carbon concentration alone does not determine the AASHTO T 21 response. The observed color is also governed by the composition, alkali solubility, and chromophoric character of the organic constituents, together with source-specific mineralogical and chemical characteristics.

The washing results provide additional evidence of this distinction. For mines 16608 and 11057, substantial reductions in organic carbon measured with MWB were accompanied by decreases in AASHTO T 21 plate number from 5 to 1. Other sources exhibited only minor changes in both measurements. These results indicate that the two methods respond to related, but not equivalent, properties of the organic matter. MWB quantifies oxidizable organic carbon, whereas AASHTO T 21 reflects the alkaline color response of soluble organic constituents. The apparent transition near 0.012% may therefore be useful for source-specific monitoring, but the available data do not justify its use as a universal statewide acceptance threshold.

4.1.4. Elemental Analyzer Total Carbon and Modified-Walkley Black

Organic carbon measured with the modified Walkley–Black method was compared with total carbon determined by elemental analysis for the unwashed samples from each mine. Each material was evaluated in bulk form and across selected sieve fractions to determine whether the distribution of carbon varied with particle size and whether the two analytical methods exhibited comparable trends.

The methods characterize different carbon fractions and should not be expected to produce equivalent numerical results. The modified Walkley–Black procedure estimates the fraction of organic carbon susceptible to dichromate oxidation, whereas elemental analysis quantifies the total carbon released during combustion. The elemental-analysis result may therefore include both organic carbon and inorganic carbon associated with carbonate minerals, shell fragments, carbonate fines, or surface coatings. Differences between the two measurements may also arise from incomplete oxidation by the modified Walkley–Black procedure, sample heterogeneity, and the contrasting analytical resolution of the methods.

The MWB and EA results are presented side by side in Table 4-5 and the relationship between the two measurements is illustrated in Figure 4-5. Although the two measurements exhibited a general positive association, they were neither analytically equivalent nor sufficiently consistent to support direct comparison or conversion. The modified Walkley–Black method estimates oxidizable organic carbon, whereas elemental analysis measures total carbon and may include inorganic carbonate-derived carbon.

Table 4-5: Organic Carbon Measured by MWB and Total Carbon Measured by EA

Mine ID	#16 Sieve		#30 Sieve		#50 Sieve		#100 Sieve		Bulk	
	MWB	EA	MWB	EA	MWB	EA	MWB	EA	MWB	EA
16564	0.0003	0	0.0003	0	0.0006	0	0.0013	0	0.0013	0
16608	0.0051	0.03	0.0056	0.01	0.0113	0.01	0.0154	0.04	0.0124	0.03
11057	0.0054	0.01	0.0066	0.01	0.0133	0.02	0.0222	0.04	0.013	0.04
61377	0.0013	0	0.002	0	0.0034	0.01	0.0033	0.01	0.0044	0.01
05455N	0.0166	0.01	0.0056	0.02	0.0077	0.02	0.0105	0.02	0.012	0.04
05455P	0.0103	0	0.0055	0	0.0072	0.01	0.0096	0.02	0.0077	0.02

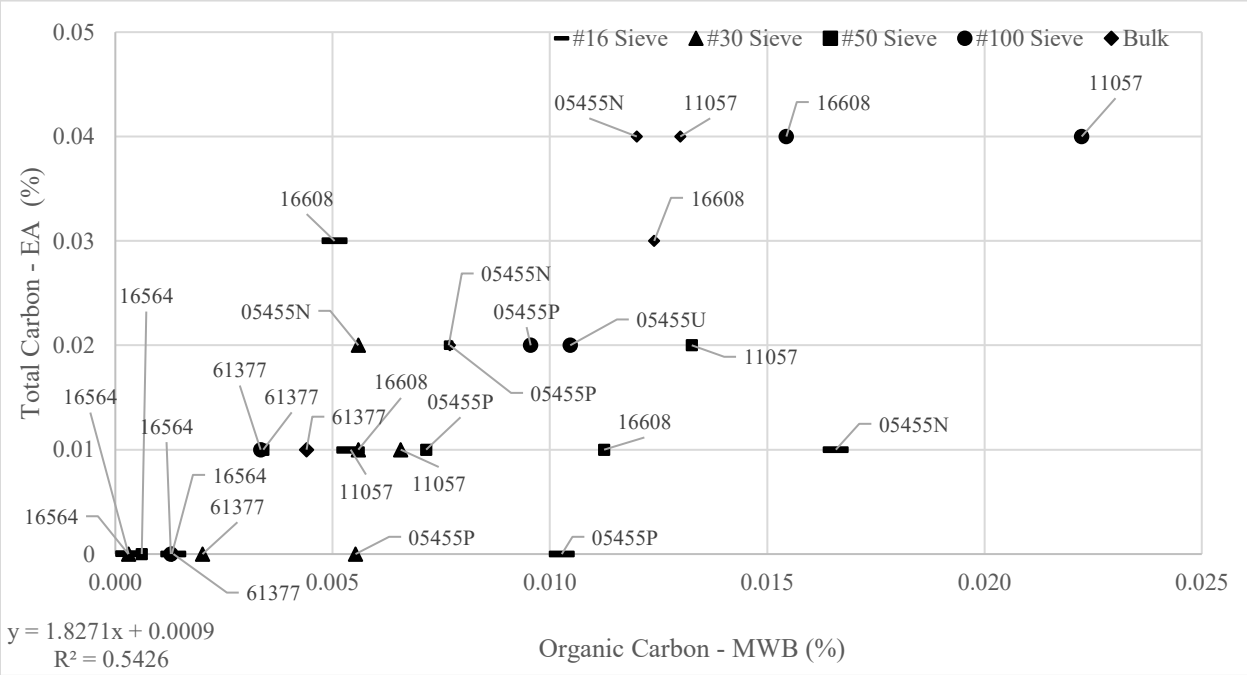

Figure 4-5: Organic Carbon (MWB) vs. Total Carbon by (EA)

The relationship between organic carbon measured with the modified Walkley–Black method and total carbon determined by elemental analysis is presented in Figure 4-5. The two measurements were positively associated, with a correlation coefficient of 0.736 and a coefficient of determination of 0.543, indicating that samples containing greater measured organic-carbon contents generally also contained greater total-carbon contents. The relationship was nevertheless insufficient to establish analytical equivalence between the methods.

The modified Walkley–Black procedure estimates the fraction of carbon susceptible to chemical oxidation under the prescribed test conditions, whereas elemental analysis quantifies total carbon without distinguishing between organic and inorganic forms. Elemental-analysis results may therefore include carbon associated with carbonate-bearing minerals or other inorganic

constituents in addition to organic carbon. Differences in analytical scope, oxidation efficiency, and the distribution of carbon among particle-size fractions consequently contribute to the variation observed between the two measurements.

4.1.5. Relationship between pH, Modified Walkley-Black and AASHTO T 21

Organic-bearing soils and fine aggregates may exhibit reduced pH as a result of organic acid formation during decomposition and the presence of acidic functional groups associated with humic substances. Prior research has shown the addition of humic and fulvic acids results in measurable decreases in pH [43], [44]. Organic acids such as tannic, humic, and acetic acids have been identified as potentially detrimental to cement hydration [27]. Previous evaluations of aggregates from mines near Clermont, FL, in proximity to mines 16564 and 16608, and near Tavares, FL, in proximity to mine 11057, have also reported the presence of humic substances. These findings suggest that regional deposits may contain comparable organic constituents capable of influencing both chemical indicators and cementitious performance [45].

The pH results for the unwashed sands and sands washed in accordance with the AASHTO T 71 procedure are summarized in Table 4-6. The data was evaluated in conjunction with MWB-measured organic carbon and AASHTO T 21 color ratings to determine whether aggregate pH provided additional insight into organic-related behavior. AASHTO T 21 provides a qualitative indication of potentially deleterious organic impurities based on alkaline color response, whereas MWB provides a quantitative measure of oxidizable organic carbon. The pH measurements provide a supplemental chemical characterization of the sand-water system but should not be interpreted as a direct measure of organic content. Rather, pH was evaluated to determine whether lower measured pH values were associated with higher MWB-measured organic carbon or more severe AASHTO T 21 color ratings.

The pH measurements and their relationships with organic-carbon content and AASHTO T 21 color response are presented in Table 4-6 and Figure 4-6 and Figure 4-7. Washing generally shifted the sands toward more alkaline conditions. Five of the six sources exhibited increases in pH, with mine 11057 showing the largest change, from 7.93 to 9.38. Mine 05455P was the only source to exhibit a slight decrease after washing. These results confirm that the AASHTO T 71 washing procedure altered the chemical condition of the sand-water system, most likely through exposure to and retention of alkalinity from the sodium hydroxide solution.

An inverse association was observed between pH and organic carbon measured with the modified Walkley–Black method. Samples with lower pH generally contained higher measured organic-carbon contents, whereas the washed samples tended to exhibit higher pH and lower organic-carbon values. The relationship was not uniform across all sources, however, demonstrating that pH alone does not quantify organic content. Aggregate mineralogy, soluble salts, carbonate buffering, fines, and the chemical character of the organic constituents may also influence the measured response.

A stronger inverse relationship was observed between pH and AASHTO T 21 color rating, with R^2=0.603. The two unwashed sands assigned a plate number of 5, mines 16608 and 11057, also

exhibited the lowest pH values in the dataset. Following washing, their pH increased and their plate ratings decreased to 1. Although this pattern is consistent with removal or alteration of acidic, alkali-soluble organic constituents, pH remains a supplemental chemical characteristic rather than an independent screening or acceptance criterion.

Table 4-6: pH of Washed and Unwashed Sand Samples

Mine ID	Unwashed 15 min pH	Washed 15 min pH
16564	8.93	9.48
16608	7.63	8.63
11057	7.93	9.38
61377	8.28	9.2
05455N	8.12	8.85
05455P	8.85	8.68

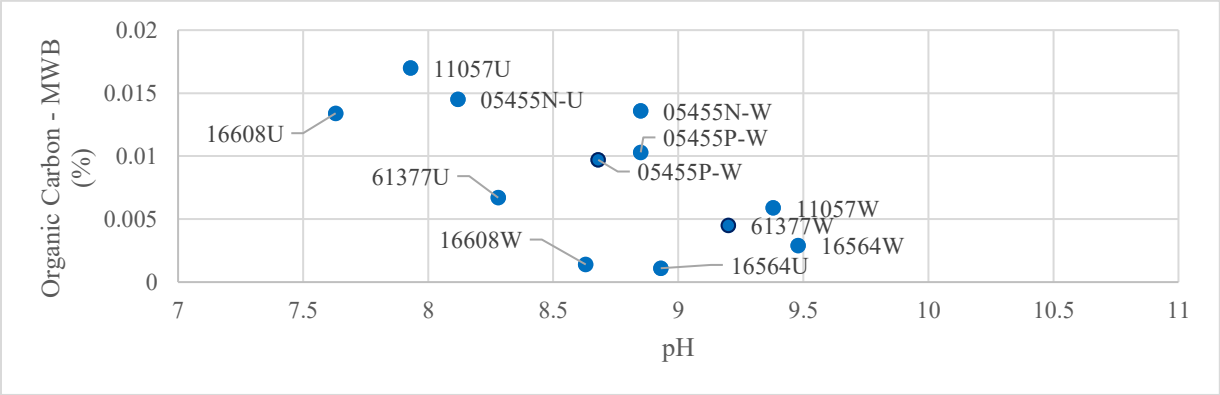

Figure 4-6: Relationship Between pH and Organic Carbon for Washed and Unwashed Sands

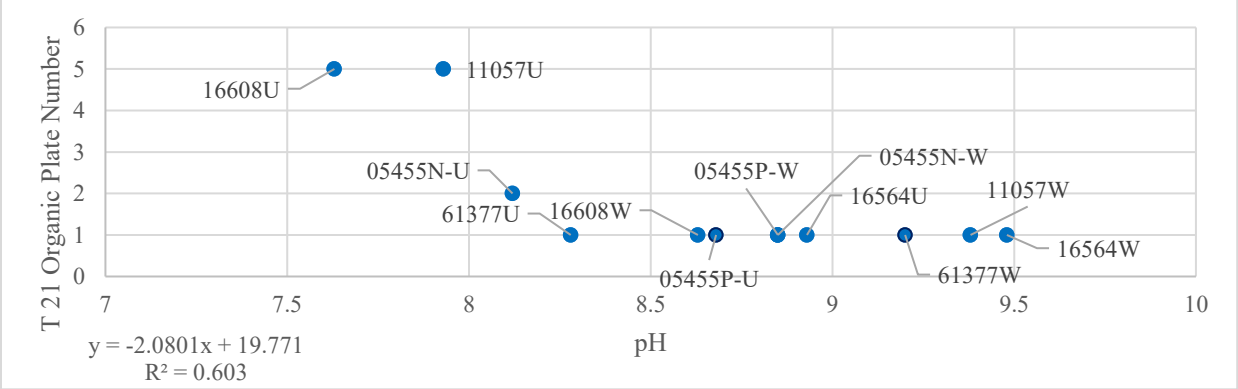

Figure 4-7: Relationship Between pH and AASHTO T 21 Color Rating for Washed and Unwashed Sands

4.1.6. Inorganic Chemical Characteristics

The inorganic composition of the natural fine aggregates was evaluated using inductively coupled plasma–atomic emission spectroscopy and X-ray fluorescence. The two methods provided complementary information: ICP-AES quantified elemental concentrations in the analyzed samples, while XRF characterized the bulk oxide composition of the sands. Together, these analyses were used to identify inorganic constituents that could potentially influence mortar strength or otherwise contribute to the observed differences among aggregate sources.

The ICP-AES results are presented in

Table 4-7 which provide values for silicon, aluminum, calcium, magnesium, iron, and selected trace elements were detected at varying concentrations across the mine sources. The overall compositions were consistent with silica-rich natural sands containing minor quantities of aluminosilicate, carbonate, and iron-bearing constituents. Although compositional differences were observed among the sources, no individual element displayed a systematic relationship with the AASHTO T 71 strength results or measured compressive strength.

X-ray fluorescence was conducted to characterize the bulk oxide composition of the natural fine aggregates and to evaluate constituents, particularly phosphorus, that were not detected or fully resolved by ICP-AES. The XRF results indicated that the sands were predominantly silica-rich and contained only minor concentrations of other inorganic oxides. Phosphorus was present at negligible to low levels across the evaluated sources, with mines 05455U and 05455W exhibiting slightly higher P_2O_5 contents than the remaining samples. The complete XRF results are presented in Table 4-8. The combined ICP-AES, XRF, and mortar-performance results therefore provide no evidence that phosphorus, or any other inorganic constituent measured in this study, exerted a measurable influence on strength development within the concentration ranges evaluated.

Table 4-7: Elemental Composition of Mine Sands Determined by Inductively Coupled Plasma–Atomic Emission Spectroscopy

Concentrations are ppm in solid samples							
Element	16564	16608	11057	61377	05455N	05455P	OttawaC
Li	5.44	4.97	5.22	5.23	4.98	4.92	4.52
Be	3.55	3.38	3.59	3.66	3.58	3.69	3.32
B	10.98	4.69	2.49	2.2	0.96	*	0.06
Cr	7.22	6.63	7.37	8.02	7.69	9.31	5.95
Co	1.02	0.92	1.1	1.02	1.11	1.07	0.94
Ni	2.03	1.75	2.25	2.21	2.19	1.99	1.83
Cu	2.9	1.7	1.5	1.8	1.3	1.3	1.6
Zn	5.53	4.42	4.74	5.16	4.73	4.86	5.31
As	3.23	2.95	2.97	3.4	3.41	3.35	3.04
Cd	1.97	1.96	1.98	2.1	2.07	2.15	1.93
Sb	2.32	2.32	2.31	2.49	2.43	2.52	2.25

Concentrations are ppm in solid samples							
Element	16564	16608	11057	61377	05455N	05455P	OttawaC
Mo	2.74	2.7	2.58	2.77	2.8	2.82	2.59
Ba	10.47	8.47	15.07	6.98	81.41	66.68	9.67
Pb	3.13	2.52	2.62	1.87	3.29	3.1	1.84
Mg	64.4	25.8	44.9	50.5	324	280	34.4
Al	4828	3096	3676	4313	5539	5057	3159
Ca	203	59	114	117	1677	1164	85
Mn	6.2	3.2	11	4.1	8.3	9.4	1.7
Fe	945	154	361	828	800	536	189

*: Below detection limit.

Table 4-8: Elemental Composition of Mine Sands Determined by X-Ray Fluorescence

Mine	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	P_2O_5	Mn_2O_3	SrO	Cr_2O_3	ZnO	xrfLOI	Total
	%	%	%	%	%	%	%	%	%	%	%	%	%	%
16564	99.3	0.12	0.74	0	0	0.01	0.05	0	0.05	0.09	0.17	0.02	0	100.6
16608	98.16	0.16	0.63	0	0	0.02	0.05	0	0.04	0.09	0.15	0.02	0.13	99.45
11057	97.93	0.38	0.69	0	0	0.06	0.09	0	0.05	0.09	0.14	0.02	0.11	99.56
61377	98.09	0.33	0.85	0	0	0.02	0.09	0	0.05	0.09	0.18	0.02	0.14	99.86
05455N	96.73	1.42	0.26	0.05	0.02	0.44	0.1	0.06	0.04	0.09	0.07	0.02	0.78	100.1
05455P	97.81	0.71	0.81	0	0	0.29	0.08	0.05	0.05	0.09	0.16	0.02	0.04	100.1

4.2. Temporal Variability of Sands

Organic carbon contents of the bulk mine samples in their as-received condition were determined using the modified Walkley–Black method, with the results summarized in Table 4-9. Temporal variability of organic Carbon was assessed using MWB test results from samples collected in 2022 and 2024. The evaluation is limited by sample availability, only two independent samples per mine were obtained across the study period, and for mines 16564, 61377, and 05455P, only a single sample exists, preventing any temporal comparison. For the remaining mines (16608, 11057, and 05455N), where both time points are available, organic Carbon values remain consistently low and show only minor fluctuations; however, the limited number of data points is insufficient to draw meaningful conclusions regarding temporal trends. A repeat test was conducted on the 2024 sample for all mines that could serve a consistency check, with differences between the two runs reflecting test repeatability rather than temporal change. The

available data does not allow for a robust characterization of organic Carbon variability over time.

Table 4-9: Organic Carbon Content Determined by the MWB for Mine Sands (2022–2025)

Mine	2022 Organic Carbon (%)	2024 Organic Carbon (%)	RETEST 2024 Organic Carbon (%)
16564	-	0.0013	0.0011
16608	0.0094	0.0124	0.0134
11057	0.0145	0.013	0.017
61377	-	0.0044	0.0067
05455N	0.0194	0.012	0.0145
05455P	-	0.0077	0.0103

4.3. Effect of AASHTO T 71 Washing on Screening Tests

Each aggregate source produced an AASHTO T 21 organic plate number of 1 after completion of the AASHTO T 71 washing procedure, as shown in Table 4-2, suggesting that organics are effectively removed from the sands under current testing conditions. To investigate this further, organic carbon was measured in the corresponding washed and unwashed materials using the modified Walkley–Black method, to determine whether washing produced a measurable reduction in organic-carbon content. pH testing was conducted in parallel, in accordance with the Florida Method of Test for pH of Soil and Water, FM 5-505 [21]. For both organic carbon and pH, a two-tailed paired t-test was conducted, with the null hypothesis stating that washing produced no effect on the measured parameter.

4.3.1. Effect on Organic Carbon Measured with the Modified Walkley–Black Method on Natural Fine Aggregates

Organic Carbon was measured both in the washed and unwashed condition. Five of the six aggregate sources exhibited lower measured organic-carbon contents after washing. The largest reductions occurred for mines 16608 and 11057, where organic carbon decreased by 0.0120 and 0.0111 percentage points, respectively. Smaller reductions were measured for mines 61377, 05455N, and 05455P. Mine 16564 represented the only exception, with measured organic carbon increasing from 0.0011% in the unwashed material to 0.0029% after washing. The mean washed-minus-unwashed difference was −0.0042 percentage points, indicating an overall reduction in measured organic carbon across the evaluated sources.

The paired t-test produced a calculated value of −1.739. The absolute magnitude of the calculated statistic remained below the critical value of 2.571 at the 95% confidence level. The null hypothesis that washing produced no systematic change in measured organic-carbon content therefore could not be rejected. The limited number of aggregate sources and the variability among the paired differences constrain the strength of the statistical inference. A dataset comprising only six paired observations provides limited power to distinguish a modest systematic reduction from source-specific variation.

The predominance of negative paired differences nevertheless provides qualitative evidence that AASHTO T 71 washing generally reduced the fraction of organic carbon measured with the

modified Walkley–Black method. The magnitude of that reduction varied considerably among sources, indicating that the effectiveness of washing depended on the concentration, chemical character, and removability of the organic constituents present. A post-washing AASHTO T 21 plate number of 1 therefore should not be interpreted as evidence that the aggregate is free of potentially deleterious organic matter. The color response and the measured organic-carbon content represent related but analytically distinct characteristics of the material.

Table 4-10: Organic Content for MWB for Washed and Unwashed Samples

Mine ID	Unwashed Organic Carbon (%)	Washed Organic Carbon (%)	Difference W-U
16564	0.0011	0.0029	0.0018
16608	0.0134	0.0014	-0.012
11057	0.017	0.0059	-0.0111
61377	0.0067	0.0045	-0.0022
05455N	0.0145	0.0136	-0.0009
05455P	0.0103	0.0097	-0.0006
Mean	0.0105	0.0063	0.0042%
Standard Deviation	0.006	0.005	0.005
		t-calculated	-1.739
		t-critical	2.571

4.3.2. Effect of Washing on pH of Natural Fine Aggregates

The pH of each sand was measured in both the unwashed condition and after washing in accordance with AASHTO T 71 and the results are in Table 4-11. The unwashed sands exhibited mildly alkaline pH values ranging from 7.63 to 8.93. Following washing, five of the six sands showed increases in pH, with measured values ranging from 8.63 to 9.48. The largest increase occurred for mine 11057, where pH increased from 7.93 to 9.38, while mine 05455P exhibited a slight decrease of 0.17 pH units. A two-tailed paired t-test confirmed that washing produced a statistically significant increase in pH at the 95% confidence level.

Table 4-11: pH of Soil and Water Using the T-71 for Washed and Unwashed Samples

Mine ID	Unwashed pH	Washed pH	Difference
16564	8.93	9.48	0.55
16608	7.63	8.63	1
11057	7.93	9.38	1.45
61377	8.28	9.2	0.92
05455N	8.12	8.85	0.73
05455P	8.85	8.68	-0.17
Mean	8.29	7.6	0.7
Standard Deviation	0.51	0.34	0.59
		t-calculated	2.639
		t-critical	2.571

4.4. Mortar Strength Performance of Natural Fine Aggregates

Mortar compressive-strength loss represents the principal performance concern associated with potentially deleterious organic impurities in natural fine aggregates. The AASHTO T 71 procedure addresses this concern by comparing mortar prepared with unwashed sand against mortar prepared with the same sand after alkaline washing. Strength results at 3, 7, and 28 days were therefore evaluated to determine whether washing produced a systematic change in mortar performance.

Paired t-tests were conducted for the full dataset. The null hypothesis for the paired comparison assumed that washing produced no change in compressive strength. Strength results then examined in relation to AASHTO T 21 color rating, MWB-measured organic carbon, pH, elemental composition, gradation, and isothermal calorimetry to determine whether the observed strength response could be associated with organic content, hydration behavior, or other source-specific material characteristics

4.4.1. Effects of Alkaline Washing on Strength Development at 3, 7 and 28 days

Strength development was evaluated at 3, 7, and 28 days to determine whether the influence of AASHTO T 71 washing changed with curing age. The results at each age were examined using paired comparisons of unwashed and washed mortar strengths. development was evaluated at 3, 7, and 28 days to determine whether the influence of washing varied with curing age.

4.4.1.1. Three Day Strength

The three-day mortar strength results are summarized in Table 4-12. Three of the six aggregate sources produced higher strengths after washing, while the remaining three produced higher strengths in the unwashed condition. The mean washed-minus-unwashed strength difference was 109 psi, with a standard deviation of 403 psi among the paired differences. The magnitude of the mean response was therefore small relative to the observed variability.

The paired t-test produced ($t=0.661$) and ($p=0.538$). Because the calculated t-statistic was lower than the critical value of (2.571) at the 95% confidence level, the null hypothesis that washing produced no systematic change in three-day strength could not be rejected.

The source-specific responses were substantial but directionally inconsistent. Mines 16564 and 16608 exhibited increases of approximately 612 and 580 psi following washing, respectively, whereas mines 11057 and 61377 exhibited reductions of approximately 190 and 350 psi. Mines 05455U and 05455W showed comparatively small changes. These results demonstrate that alkaline washing did not produce a uniform effect on three-day mortar strength across the evaluated sources. The observed differences are more appropriately attributed to source-specific material response and testing variability than to a consistent influence of the washing procedure.

Table 4-12: Three-Day Mortar Cube Strengths for AASHTO T-71 for Unwashed and Washed Conditions

Mine ID	Unwashed (psi)	Washed (psi)	Ratio (U/W) (%)
16564	2888	3500	82
16608	2890	3470	83

Mine ID	Unwashed (psi)	Washed (psi)	Ratio (U/W) (%)
11057	2780	2590	107
61377	3480	3130	111
05455U	3160	3080	103
05455W	3130	3210	98
Mean	3055	3163	109
Standard Deviation	256	331	403
		t-calculated	0.66
		t-critical	2.571

4.4.1.2. Seven Day Strength

The seven-day mortar strength results, summarized in Table 4-13, indicate that the evaluated sands generally maintained satisfactory performance in both the unwashed and washed conditions. Four of the six sources produced unwashed-to-washed strength ratios of at least 98%, and five remained within approximately 2 percentage points of the 95% criterion or exceeded it. Mine 05455P was the only source to fall below the criterion, with a ratio of 93%, while mines 11057 and 61377 produced ratios greater than 100%, indicating higher strength in the unwashed condition. rejected.

The mean washed-minus-unwashed strength difference was (-45) psi, compared with a standard deviation of 275 psi for the paired differences. The paired t-test produced (t=-0.400), which was substantially lower in magnitude than the critical value of (2.571) at the 95% confidence level. Accordingly, the null hypothesis that washing produced no systematic change in seven-day strength could not be rejected.

The source-specific responses were modest and bidirectional. Mines 16564 and 16608 gained 100 psi following washing, mine 05455P gained 310 psi, and mine 05455N changed by only 40 psi. In contrast, mines 11057 and 61377 each lost 370 psi after washing. This distribution confirms that the washing procedure did not produce a consistent increase or decrease in seven-day strength across the evaluated sources. Rather, the results were generally adequate, and the observed differences were more consistent with source-specific material behavior and ordinary testing variability than with a systematic effect of alkaline washing.

Table 4-13: Seven-Day Mortar Cube Strengths for AASHTO T-71 for Unwashed and Washed Conditions

Mine ID	Unwashed (psi)	Washed (psi)	Ratio (U/W)	Difference W-U
16564	4110	4210	98%	100
16608	4080	4180	98%	100

Mine ID	Unwashed (psi)	Washed (psi)	Ratio (U/W)	Difference W-U
11057	3550	3180	112%	-370
61377	4440	4070	109%	-370
05455N	3880	3840	101%	-40
05455P	3910	4220	93%	310
Mean	3995	3950		-45
Standard Deviation	296	403		275
			t-calculated	-0.4
			t-critical	2.571

4.4.1.3. 28 Day Strength

he 28-day mortar strength results are summarized in Table 4-14. Four of the six aggregate sources produced lower strengths after washing, while the remaining two produced higher strengths. The mean washed-minus-unwashed strength difference was (-273) psi, with a standard deviation of 424 psi among the paired differences. The magnitude of the mean response was therefore modest relative to the observed variability.

The paired t-test produced (t=-1.57). Because the absolute value of the calculated t-statistic was lower than the critical value of (2.571) at the 95% confidence level, the null hypothesis that washing produced no systematic change in 28-day strength could not be rejected.The source-specific responses were substantial but directionally inconsistent. Washing reduced 28-day strength by 580 psi for mine 16608, 460 psi for mine 61377, 800 psi for mine 05455N, and 196 psi for mine 05455P. In contrast, washing increased strength by 60 psi for mine 16564 and 340 psi for mine 11057. These results demonstrate that alkaline washing did not produce a uniform increase or reduction in 28-day mortar strength across the evaluated sources. The observed differences are more appropriately interpreted as source-specific material responses than as evidence of a consistent effect of the washing procedure.

Table 4-14: 28-Day Mortar Cube Strengths for AASHTO T-71 for Unwashed and Washed Conditions

Mine ID	Unwashed (psi)	Washed (psi)	Ratio (U/W)	Difference W-U
16564	5980	6040	99%	60
16608	6050	5470	111%	-580
11057	4700	5040	93%	340
61377	5920	5460	108%	-460
05455N	6260	5460	115%	-800
05455P	5450	5254	104%	-196
Mean	5727	5454		-273
Standard Deviation	569	333		424
			t-calculated	-1.57

t-critical	2.571

4.4.1.4. Summary of Washing Effects on Mortar Strength Across Curing Ages

AASHTO T 71 is confirmed as a viable final performance-based indicator, as alkaline washing produced no statistically significant or directionally consistent change in mortar compressive strength at any curing age. Paired t-tests failed to reject the null hypothesis at 3, 7, and 28 days, and the source-specific differences reversed direction between mines at every age, showing no qualitative pattern of increase or decrease. This lack of both statistical significance and directional consistency indicates that the observed variability was due to source-specific material behavior and ordinary testing variability, not to any effect introduced by washing. While washing did increase the pH of the sand in an aqueous solution, this shift did not correspond to any change in mortar strength.

This conclusion is further supported by the organic-carbon and AASHTO T 21 findings presented in the preceding sections, which indicate that the washing procedure did remove organic matter. AASHTO T 21 plate numbers returned to 1 for every source after washing, and organic-carbon content measured with the modified Walkley–Black method decreased for five of six sources. Although the paired t-test could not reject the null hypothesis at the 95% confidence level, the consistent direction of the reduction suggests a real effect that the limited sample size ($n = 6$) was underpowered to confirm statistically. Together, these results indicate that washing removed organic matter without independently altering mortar strength, establishing T 71 as a sound basis for isolating the performance effect of organic impurities.

4.4.2. Relationship Between Screening Results and Mortar Strength

4.4.2.1. AASHTO T 21

The relationship between the seven-day AASHTO T 71 unwashed-to-washed strength ratio and the AASHTO T 21 organic plate number is presented in Figure 4-8. The linear fit produced a coefficient of determination of 0.117, indicating that variation in plate number accounted for a limited portion of the observed variation in strength ratio.

Aggregate sources produced the same AASHTO T 21 plate number exhibited markedly different strength ratios. Mines 16564, 61377, and 05455P each received a plate number of 1, yet their seven-day U/W ratios ranged from approximately 93% to 109%. Similarly, mines 16608 and 11057 both received a plate number of 5 but produced U/W ratios of approximately 98% and 112%, respectively. Higher plate numbers therefore did not correspond consistently to lower relative mortar strength across the evaluated sources. The results demonstrate that the AASHTO T 21 color classification did not provide a consistent statewide indication of seven-day mortar strength performance. The method should therefore remain a qualitative screening procedure rather than a universal quantitative predictor of strength response. Its greater value may lie in source-specific monitoring, where changes in plate number are evaluated relative to the established historical response of an individual mine. A departure from the normal source-specific range may then be used to trigger additional characterization or AASHTO T 71 performance testing.

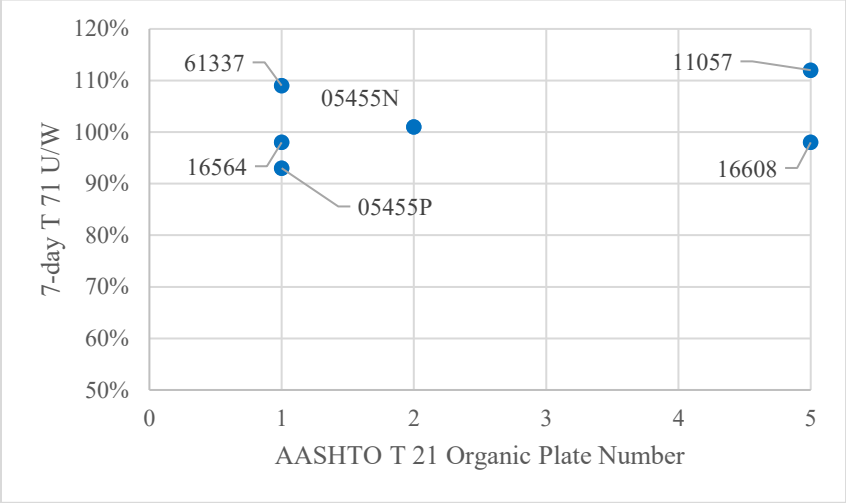

Figure 4-8: Seven-Day AASHTO T 71 Unwashed-to-Washed Strength Ratio vs. Plate Number

The relationship between the 28-day AASHTO T 71 unwashed-to-washed strength ratio and the AASHTO T 21 organic plate number is presented in Figure 4-9. The linear fit produced a coefficient of determination of 0.0366, indicating that variation in plate number accounted for essentially none of the observed variation in 28-day strength ratio.

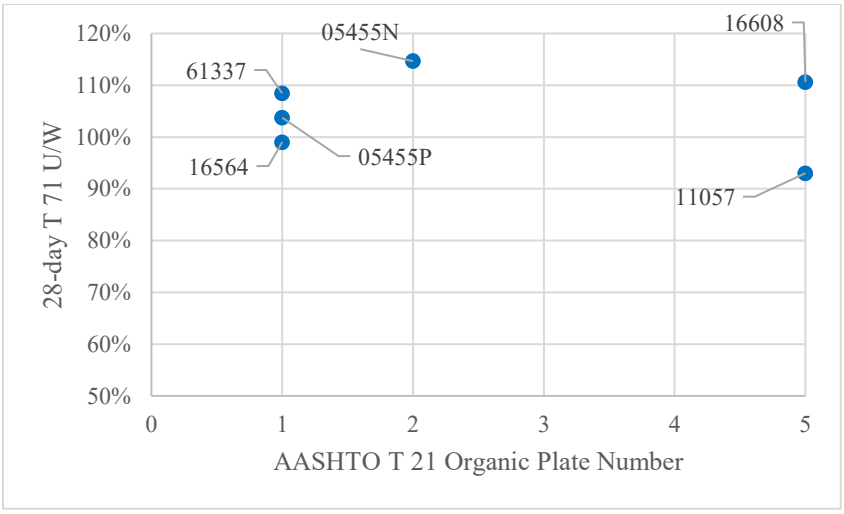

Figure 4-9: 28-Day T 71 (Unwashed/Washed) Ratio vs. AASHTO T 21 Organic Plate Number.

Sources that produced the same plate number exhibited substantially different strength responses. Mines 16564, 61377, and 05455P each produced a plate number of 1, yet their 28-day U/W ratios ranged from approximately 99% to 108%. Mines 16608 and 11057 both produced a plate number of 5 but exhibited markedly different U/W ratios of approximately 111% and 93%, respectively. Mine 05455N, which produced a plate number of 2, exhibited the highest U/W ratio at approximately 115%. Higher AASHTO T 21 plate numbers therefore did not correspond consistently to lower relative mortar strength across the evaluated sources.

These results demonstrate that the AASHTO T 21 color classification did not provide a reliable statewide indication of 28-day mortar strength performance. The method should remain a qualitative screening procedure rather than a universal quantitative predictor of strength response. Its greater value lies in source-specific monitoring, where changes in plate number are evaluated relative to the established historical behavior of an individual mine. A departure from the normal source-specific range may then be used to trigger additional characterization or AASHTO T 71 performance testing.

The 28-day results are consistent with the seven-day findings. At both ages, sources producing the same plate number exhibited markedly different U/W strength ratios, and higher plate numbers did not correspond systematically to reduced relative strength. This consistency reinforces the conclusion that AASHTO T 21 is appropriate as a qualitative screening method, but not as a direct predictor of mortar strength performance across unrelated aggregate sources.

4.4.2.2. Modified Walkley-Black

The relationship between organic carbon measured using MWB and the AASHTO T 71 unwashed-to-washed strength ratio at 7 and 28 days is presented in Figure 4-10 and Figure 4-11. At both ages, the data exhibited substantial scatter and a lacked a statistical relationship between measured organic-carbon content and relative mortar strength. At 7 days, the linear fit produced an R^2 value of 0.0868, indicating that MWB-measured organic carbon accounted for less than 9% of the observed variation in the U/W strength ratio. The 28-day results showed the same general behavior: sands with similar MWB values produced markedly different strength ratios, while increasing organic-carbon measurements did not correspond consistently to a reduction in relative strength.

Several source-specific results illustrate this limitation. Mines 16608, 11057, and 05455N exhibited among the highest MWB-measured organic-carbon contents, yet their strength responses differed substantially. At 28 days, mines 16608 and 05455N produced U/W ratios greater than 110%, whereas mine 11057 produced a ratio of approximately 93%. Conversely, mine 61377 exhibited a comparatively low MWB value but produced U/W ratios greater than 100% at both ages. These results demonstrate that MWB-measured organic carbon, considered independently, did not predict either the magnitude or direction of mortar strength response.

The absence of a consistent relationship reflects both the nature of the measured parameter and the limitations of the method at the low organic-carbon concentrations encountered from Florida sand in various mines. The MWB procedure estimates oxidizable organic carbon but does not identify the type, solubility, molecular structure, or cement-reactivity of the organic compounds present. Equal measured carbon contents may therefore represent markedly different organic assemblages and may not produce comparable effects on cement hydration or strength. In addition, the low concentrations and relatively small differences among samples approach the practical precision of the method, limiting its ability to distinguish minor changes in organic-carbon content with sufficient confidence for aggregate acceptance decisions.

Accordingly, MWB should not be used as a universal quantitative acceptance criterion, as a direct predictor of AASHTO T 71 strength performance, or as a statewide threshold applicable across independent aggregate sources. The method may, however, provide value as a supplemental source-specific monitoring tool. Repeated testing can be used to establish the characteristic MWB response and expected range of variability for an individual mine. Subsequent results may then be compared with that baseline to identify substantial departures from normal production. Such a departure should be interpreted as an indication that additional evaluation is warranted, rather than as direct evidence that the sand is deleterious. Confirmation should rely on a performance-based method, such as isothermal conduction calorimetry or AASHTO T 71 mortar strength testing.

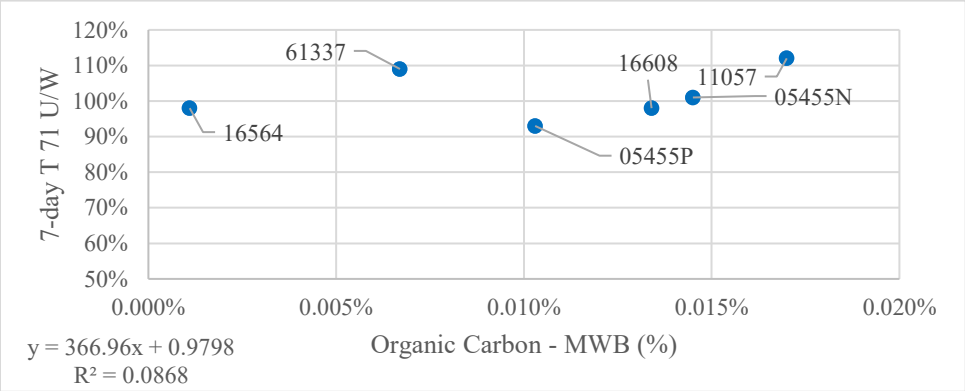

Figure 4-10: 7-Day T 71 Unwashed/Washed Ratio vs. Organic Carbon (MWB)

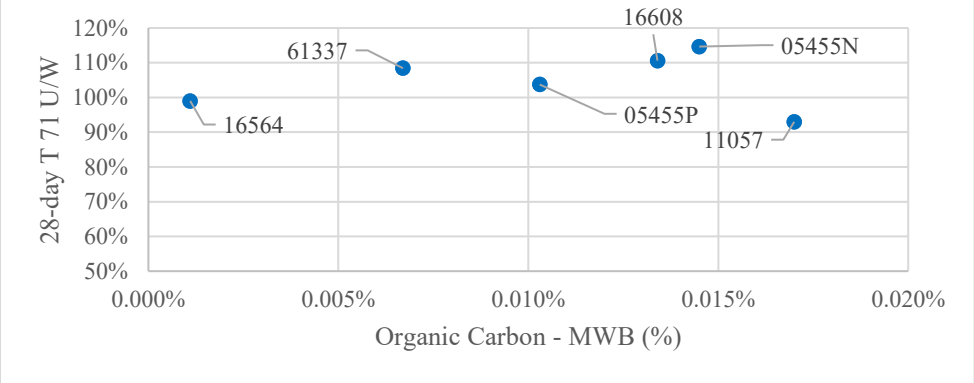

Figure 4-11: 28-Day T 71 Unwashed/Washed Ratio vs. Organic Carbon (MWB)

4.4.2.3. pH

The relationships between sand pH and the AASHTO T 71 unwashed-to-washed strength ratio at 7 and 28 days are presented in Figure 4-12 and Figure 4-13. Sand pH explained only a limited portion of the variation in relative mortar strength, with coefficients of determination of 0.205 at 7 days and 0.075 at 28 days, demonstrating that differences in measured pH accounted for only a small portion of the variation in relative mortar strength.

Aggregate sources with comparable pH values produced substantially different U/W strength ratios. Conversely, sources spanning the measured pH range did not exhibit a systematic increase or decrease in relative strength. Mines 16564 and 05455P, for example, exhibited among the highest pH values but produced distinctly different seven-day strength ratios. At 28 days, mine 16608 exhibited one of the lowest measured pH values and a U/W ratio greater than 110%, whereas mine 11057, with a moderately higher pH, produced the lowest U/W ratio in the dataset. The measured pH therefore did not account for either the magnitude or direction of the differences in mortar compressive strength.

This absence of correspondence is consistent with the nature of the measurement. The pH of an aggregate–water suspension reflects the combined influence of soluble salts, organic acids, carbonate buffering, mineralogy, fines, and residual processing constituents. It does not isolate organic content, identify the chemical character of the organic matter present, or quantify its interaction with cement hydration. Accordingly, pH was treated as a supplemental chemical characteristic rather than as a screening method, acceptance criterion, or predictor of AASHTO T 71 mortar strength.

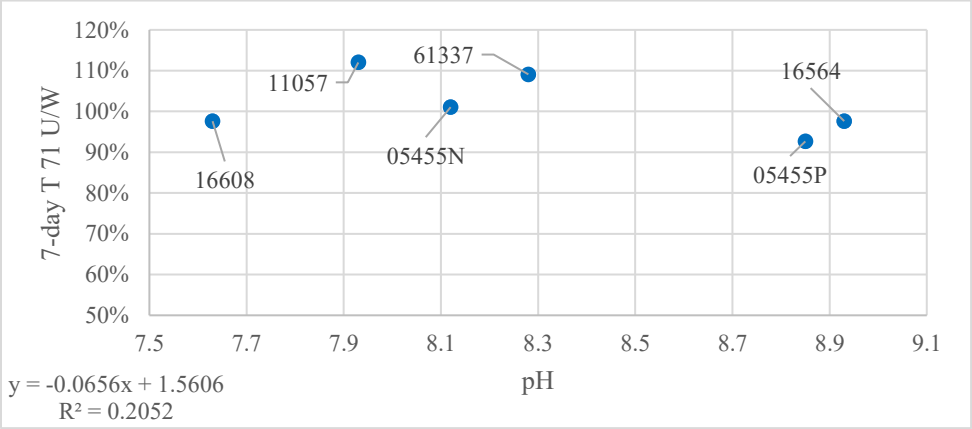

Figure 4-12: 7-Day T 71 (Unwashed/Washed) Ratio vs. pH

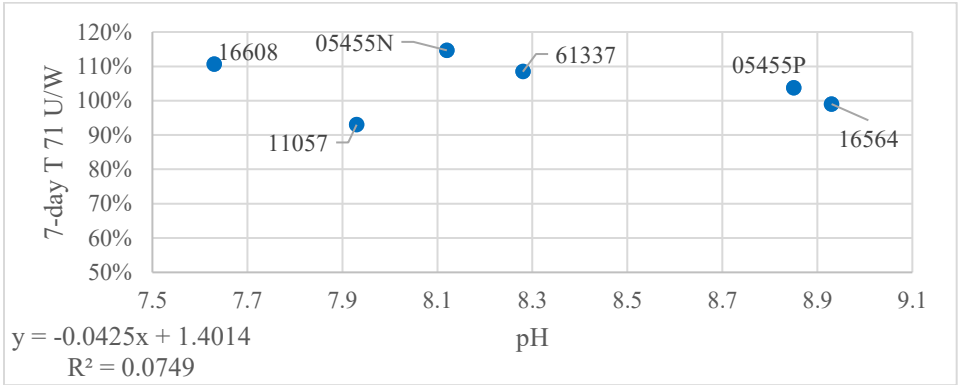

Figure 4-13: 28-Day T 71 (Unwashed/Washed) Ratio vs. pH

4.4.2.4. Influence of Organic Carbon and pH on 28-Day Compressive Strength

One of the principal objectives of this research was to determine whether the organic matter present in natural fine aggregates could be characterized in a manner that was meaningfully related to mortar performance. Organic carbon measured with the modified Walkley–Black method was therefore compared directly with 28-day mortar compressive strength to determine whether increasing organic-carbon content corresponded to a measurable reduction in strength. The pH of the aggregate–water suspension was evaluated separately as a potential supplemental indicator because acidic organic constituents may influence the chemical condition of the suspension and could, in principle, provide an indirect indication of materials associated with reduced mortar strength.

The relationship between organic carbon measured with the modified Walkley–Black method and 28-day mortar compressive strength is presented in Figure 4-14. The coefficient of determination is 0.043, confirming that measured organic-carbon content explained essentially none of the variation in compressive strength among the evaluated aggregate sources. Materials with comparable organic-carbon contents developed markedly different strengths, while materials with substantially different organic-carbon contents produced similar strengths. Within the range represented by the natural fine aggregates, increasing organic-carbon content did not correspond to a systematic reduction in 28-day compressive strength.

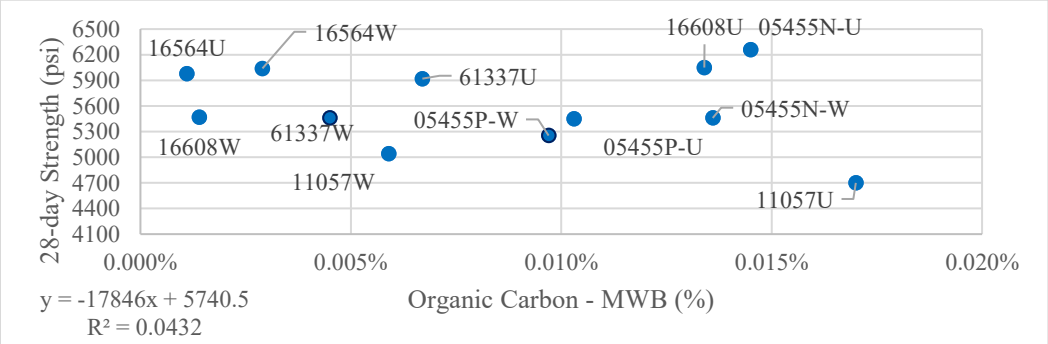

Figure 4-14: 28-Day Compressive Strength vs. Organic Carbon (MWB)

The relationship between the pH of the aggregate–water suspension and 28-day compressive strength, presented in Figure 4-15 is weaker. The coefficient of determination was 0.015, and no systematic increase or decrease in strength occurred across the measured pH range. Changes in pH resulting from the AASHTO T 71 washing procedure were not accompanied by consistent changes in compressive strength.

Neither organic carbon measured with the modified Walkley–Black method nor the pH of the aggregate–water suspension explained the observed differences in 28-day mortar compressive strength. Those differences more likely reflect the combined influence of source-specific characteristics, including gradation, fines content and distribution, particle packing, aggregate surface condition, mineralogy, and chemical constituents not isolated by either measurement. Organic-carbon content remains relevant to the characterization of potentially deleterious organic

matter, while pH may provide supplemental chemical information; neither parameter, however, can replace direct mortar testing when compressive strength governs aggregate qualification.

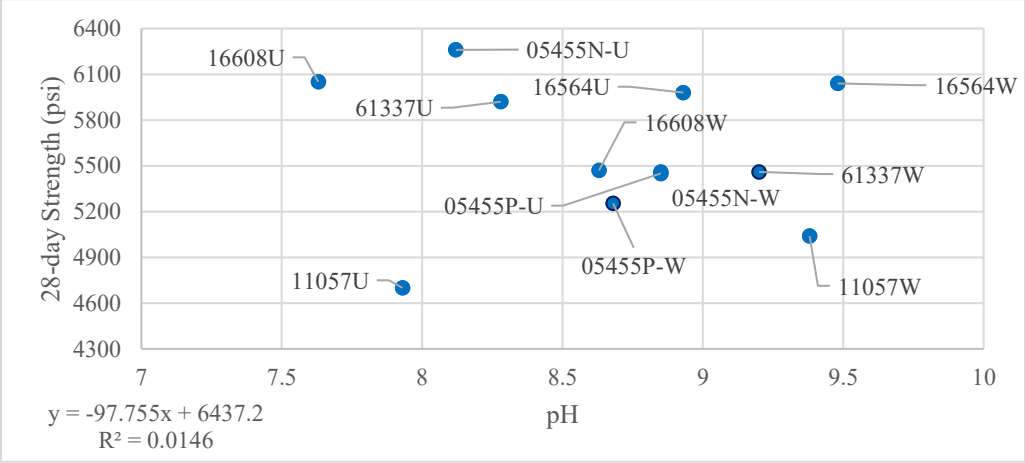

Figure 4-15: 28-Day Compressive Strength vs. pH

4.5. Isothermal Calorimetry of Natural Fine Aggregates

Isothermal conduction calorimetry provides a highly sensitive measure of cement hydration through the continuous determination of heat-flow rate under controlled temperature conditions. The resulting heat-flow curve resolves small changes in the induction period, the onset of accelerated hydration, and the development of the principal silicate peak with substantially greater temporal precision than compressive-strength measurements alone. This sensitivity makes the method particularly valuable for identifying subtle interactions between cement and constituents associated with the fine aggregate. Interpretation must nevertheless distinguish among the possible influences of organic compounds, soluble salts, fines content, particle surface area, mineralogy, and other source-specific characteristics.

Isothermal conduction calorimetry characterizes cement hydration through two related measurements: thermal power and cumulative heat. Thermal power represents the instantaneous rate of heat evolution and therefore provides the more sensitive measure of changes in hydration kinetics. The power curves for the evaluated natural fine aggregates are presented in Figure 4-16. Their general form reflects the characteristic sequence of early dissolution, induction, accelerated silicate hydration, and subsequent deceleration. The similarity of these curves indicates that the aggregate sources did not fundamentally alter the sequence of cement hydration, although differences in the timing and magnitude of the principal silicate peak reveal source-specific changes in the rate at which hydration progressed.

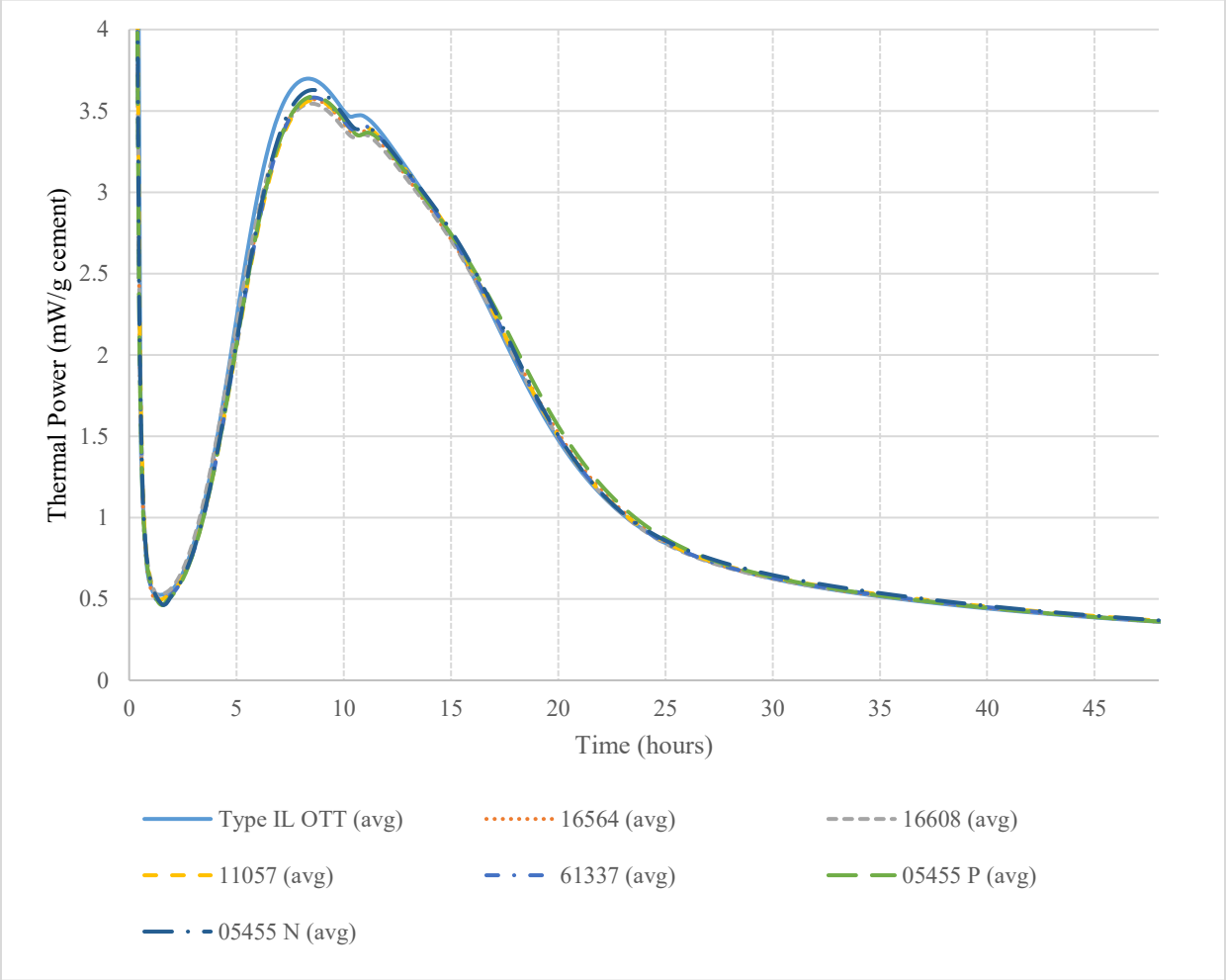

Figure 4-16: Isothermal Calorimetry Heat Flow of Mortar Prepared with Mine Sands and ASTM C778 Standard Graded Sand. Average of Duplicates.

Cumulative heat represents the integral of thermal power with respect to time and is presented in Figure 4-17. Whereas the power curve identifies when heat is being evolved and the rate at which that evolution occurs, the cumulative heat curve records the total thermal energy released through each measured interval. The close grouping of the cumulative heat curves indicates that the differences evident in Figure 4-16 were principally associated with hydration kinetics rather than with large differences in the overall extent of reaction during the test period.

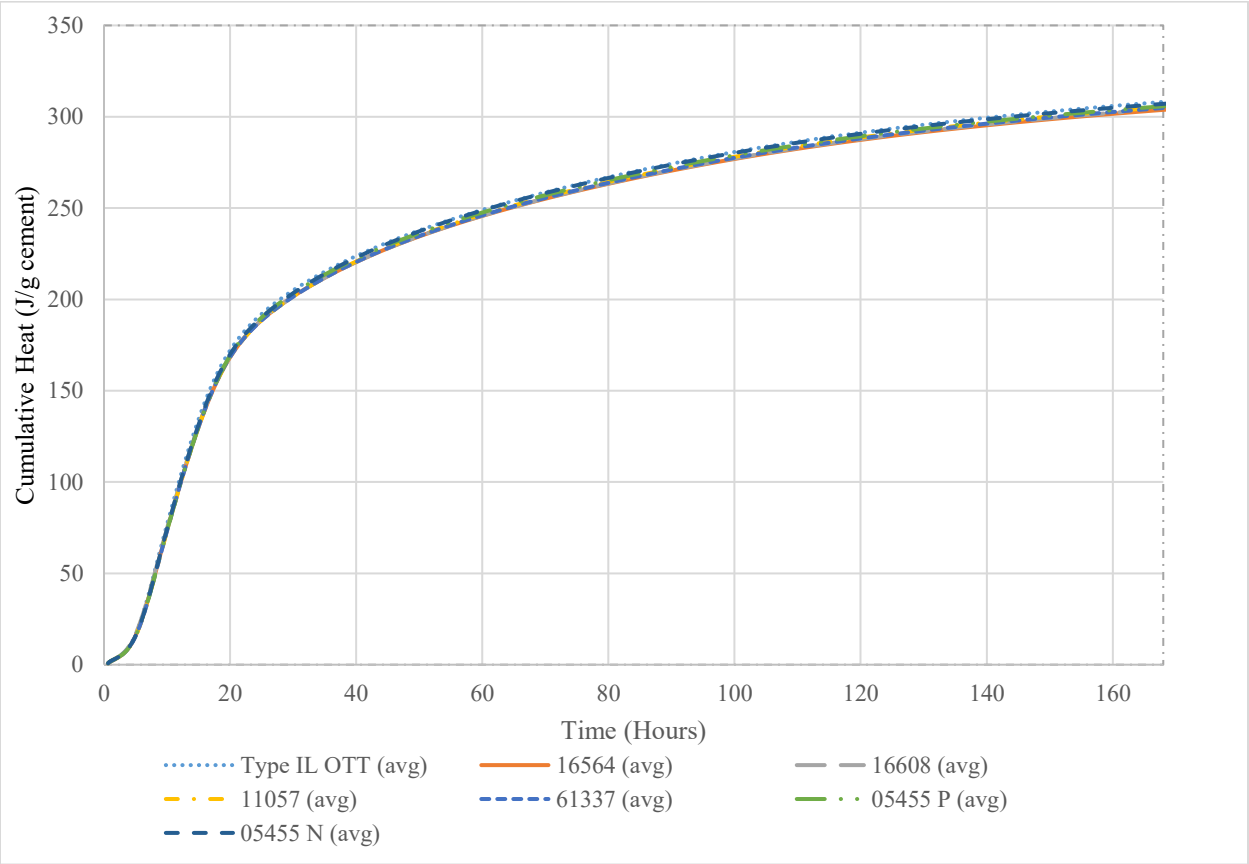

Figure 4-17: Cumulative Heat Release of Mortar Prepared with Mine Sands and ASTM C778 Standard Graded Sand. Average of Duplicates

The principal parameters extracted from the isothermal conduction calorimetry results are presented in Table 4-15. The parameters include the magnitude of the principal silicate hydration peak, the elapsed time required to reach that peak, and the cumulative heat released over the selected measurement intervals. Collectively, they characterize the maximum rate of the principal silicate reaction, the timing of the transition into accelerated hydration, and the integrated progression of hydration with time.

The magnitude of the principal silicate peak defines the maximum thermal power attained during accelerated hydration, whereas the corresponding peak time reflects the duration of the preceding induction period. Cumulative heat, obtained through integration of thermal power with respect to time, quantifies the total heat released through each selected interval. Evaluation of these parameters in combination permits differentiation among delayed hydration, suppression of the maximum reaction rate, and persistent reductions in the overall progression of hydration. The time to the principal silicate peak provides a distinct measure of the duration of the induction period and the onset of accelerated hydration. A delayed peak signifies that the system required a longer interval to enter the principal stage of silicate reaction. Peak timing and peak magnitude must therefore be interpreted together. Similar peak magnitudes may occur after substantially

different induction periods, while comparable peak times may be followed by different maximum heat-flow rates.

The cumulative heat values reported in Table 4-15 provide the corresponding measure of reaction progression. A mixture may exhibit a delayed or reduced principal peak yet subsequently approach the cumulative heat of the other mixtures, indicating that the early alteration in hydration rate was not sustained. Persistently lower cumulative heat would instead indicate that the reduction extended beyond the timing or magnitude of the principal peak. The parameters reported in Table 4-15 consequently provide complementary information: peak time defines the onset of accelerated hydration, peak magnitude defines the maximum reaction rate, and cumulative heat defines the integrated progression of hydration.

Table 4-15: Key Hydration Parameters Determined from Isothermal Calorimetry

Mine ID	Main Calcium Silicate Peak Heat (mW/g)	Main Calcium Silicate Peak Time (h)	Secondary Aluminate Peak Power (mW/g)	Secondary Aluminate Peak Time (h)	Cumulative Heat (J/g) @ 72 hours	Cumulative Heat (J/g) @ 168 hours	Cumulative Heat (J/g) @ 405 hours
OTT	3.7	8.35	3.47	10.86	260.42	308.13	341.19
16564	3.57	8.55	3.38	11.06	256.81	303.74	334.16
16608	3.55	8.55	3.36	10.89	256.99	304.34	335.1
11057	3.57	8.63	3.4	10.98	257.74	305.27	336.02
61377	3.58	8.55	3.41	10.89	257.26	304.79	335.68
05455U	3.63	8.61	3.4	11.01	260.04	307.04	337.33
05455W	3.59	8.61	3.37	11.17	258.84	305.74	336.07

Mine 11057, which failed AASHTO T 21, passed T 71 at 7 days but failed at 28 days, does not exhibit a corresponding reduction in cumulative heat, which remains near the midpoint of the dataset at both 7 and 19 days. This indicates that the observed transition from relatively high strength at 7 days to low strength at 28 days is not associated with a decrease in overall hydration extent. In terms of reaction characteristics, both Mines 11057 and 16608, which failed T 21 and also exhibited the highest organic Carbon contents measured by modified Walkley–Black, show among the lowest calcium silicate peak magnitudes, with 11057 exhibiting the most retarded reaction behavior. This is consistent with the mechanism discussed in Section 3, where organic constituents are expected to primarily retard the rate of hydration reactions rather than reduce the total degree of hydration. Accordingly, the calorimetry results suggest a subtle kinetic delay associated with elevated organic content, although the effect is not sufficiently large to influence cumulative heat or early-age strength development.

Additional calorimetric evaluation was performed on mines 16608 and 11057 after both sources failed the initial AASHTO T 21 assessment. Organic carbon measured with the modified

Walkley–Black method was concentrated principally within the material passing the No. 100 sieve, where values of 0.0154% and 0.0222% were measured for mines 16608 and 11057, respectively. The calorimetric program therefore included both the bulk aggregate and the isolated No. 100 fraction from each source to determine whether the fraction containing the greatest organic-carbon concentration exerted a distinguishable influence on cement hydration. The thermal-power curves are presented in Figure 4-18, the corresponding cumulative-heat curves are presented in Figure 4-19, and the principal calorimetric parameters are summarized in Table 4-16.

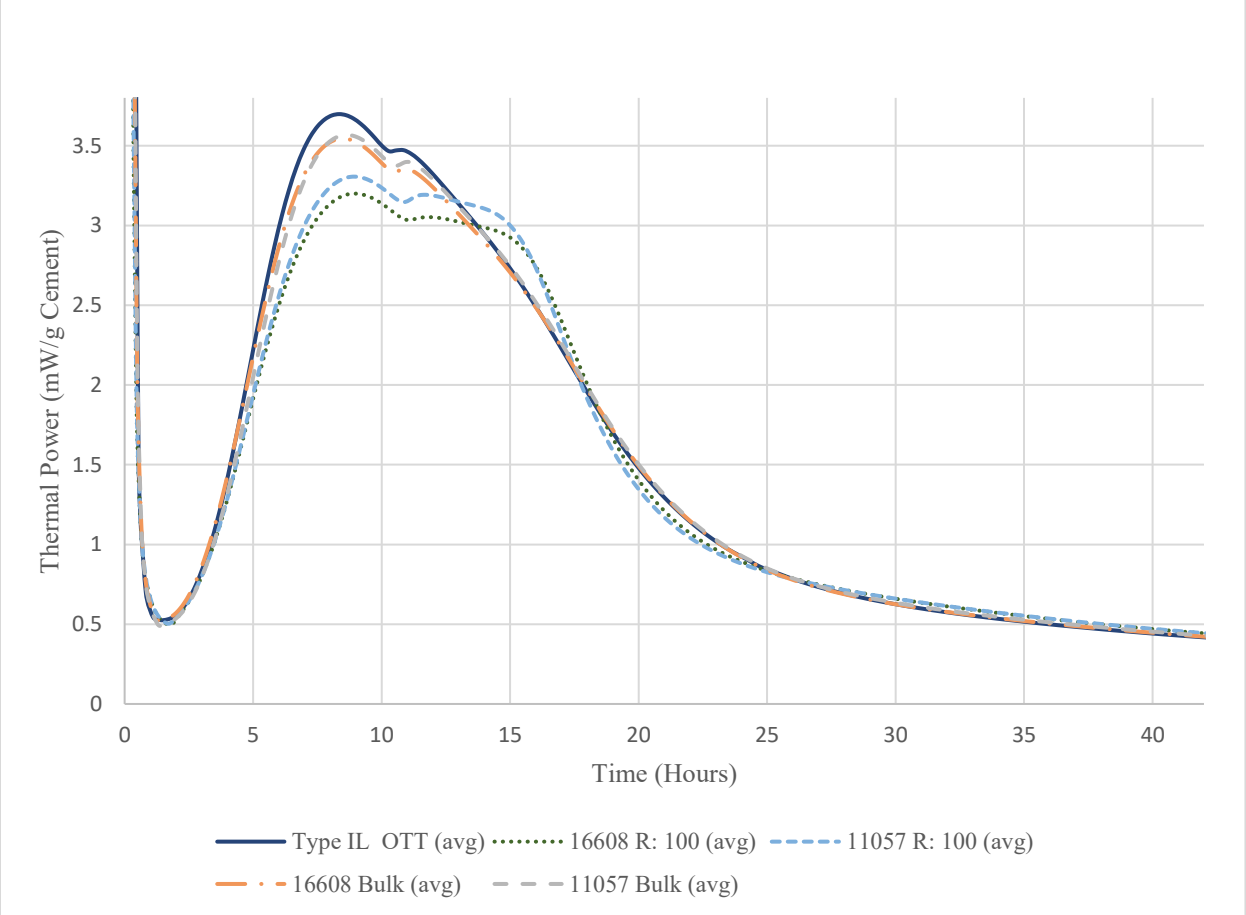

Figure 4-18: Isothermal Calorimetry Heat Flow of Cement Paste Prepared with No. 100 Sieve Sand Fraction and Bulk of Mines 16608 and 11057, Compared to Control Sample Made with ASTM C778 Standard Graded Sand. Average of Duplicates

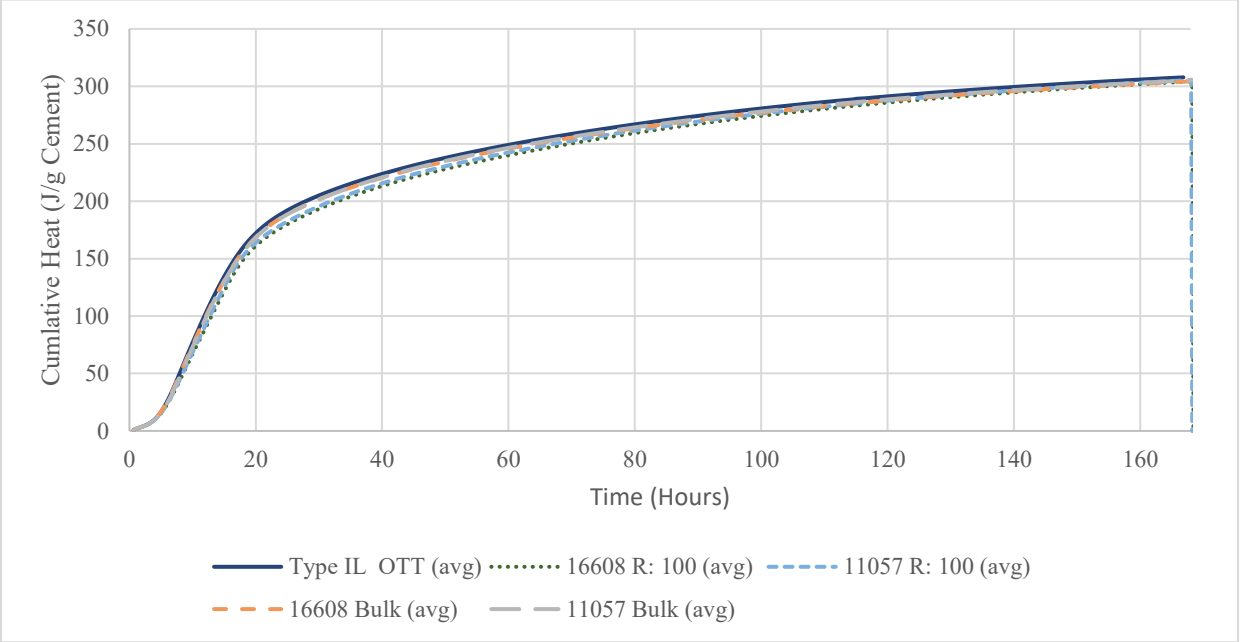

Figure 4-19: Isothermal Calorimetry Cumulative Heat of Cement Paste Prepared with No. 100 Sieve Sand Fraction and Bulk of Mines 16608 and 11057, Compared to Control Sample Made with ASTM C778 Standard Graded Sand. Average of Duplicates

The bulk materials from mines 16608 and 11057 produced hydration profiles that remained broadly comparable with the ASTM C778 standard graded-sand control. The principal calcium silicate peak powers were 3.55 and 3.57 mW/g for mines 16608 and 11057, respectively, compared with 3.70 mW/g for the control. Peak times were similarly close, occurring at 8.55 hours for mine 16608, 8.63 hours for mine 11057, and 8.35 hours for the control. These differences indicate a modest reduction in the maximum rate of silicate hydration and a slight extension of the induction period, but neither bulk aggregate produced a substantial departure from the hydration kinetics of the control mixture.

A more pronounced distinction emerged when the isolated No. 100 fractions were evaluated. The principal silicate peak power decreased to 3.20 mW/g for mine 16608 and 3.31 mW/g for mine 11057, while the corresponding peak time increased to 8.97 hours for both materials. The secondary aluminate peak exhibited the same general tendency. Peak power declined from 3.36 to 3.05 mW/g for mine 16608 and from 3.40 to 3.19 mW/g for mine 11057, accompanied by delays from 10.89 to 12.15 hours and from 10.98 to 11.98 hours, respectively. Concentration of the finer aggregate fraction therefore produced a measurable reduction in peak intensity and a discernible delay in both the principal silicate and secondary aluminate reactions.

The cumulative-heat results provide an important qualification to the reductions observed in thermal power. At 72 hours, cumulative heat for the sand passing the No. 100 sieve was lower than that of the corresponding bulk materials and the control, reflecting the slower early progression of hydration. By 168 hours, however, the cumulative heat values had largely converged. Mine 16608 produced 304.34 J/g for the bulk aggregate and 304.30 J/g for the No.

100 sieve, while mine 11057 produced 305.27 and 305.50 J/g, respectively. The control reached 308.13 J/g. The near-equivalence of the 168-hour values demonstrates that the reductions in peak power and delays in peak timing represented temporary modifications to hydration kinetics rather than sustained suppression of the overall reaction.

The No. 100 fractions from mines 16608 and 11057 consequently exerted a greater influence on early hydration than the corresponding bulk aggregates. That influence was expressed through lower silicate and aluminate peak powers, delayed peak development, and reduced cumulative heat at 72 hours. The subsequent convergence in cumulative heat indicates that hydration continued after the initial delay and approached an extent comparable with the bulk aggregates and control. These results establish that the fraction containing the highest measured organic-carbon concentration was also the fraction most capable of altering early hydration kinetics; they do not, however, establish organic carbon as the sole cause of the observed changes. The greater specific surface area, mineralogical composition, soluble constituents, and other chemical characteristics of the No. 100 fraction may also have contributed to the measured differences.

Table 4-16: Key Hydration Parameters of Isothermal Calorimetry Prepared with No. 100 Sieve Sand Fraction and Bulk of Mines 16608, 11057 and Control

Mine ID	Main Calcium Silicate Peak Power (mW/g)	Main Calcium Silicate Peak Time (h)	Secondary Aluminate Peak Heat (mW/g)	Secondary Aluminate Peak Time (h)	Cumulative Heat (J/g) @ 72 hours	Cumulative Heat (J/g) @ 168 hours
16608	3.55	8.55	3.36	10.89	256.99	304.34
16608 #100	3.20	8.97	3.05	12.15	252.21	304.30
11057	3.57	8.63	3.40	10.98	257.74	305.27
11057 #100	3.31	8.97	3.19	11.98	254.54	305.50
OTT	3.70	8.35	3.47	10.86	260.42	308.13

The calorimetric results establish that the most pronounced changes in early hydration occurred when the isolated No. 100 fractions from mines 16608 and 11057 were introduced into the cementitious system. Relative to the corresponding aggregate sources, these fractions produced lower silicate- and aluminate-peak powers, delayed peak development, and reduced cumulative heat at 72 hours. The subsequent convergence in cumulative heat indicates that hydration continued after the initial delay and ultimately approached the reaction extent measured for the corresponding aggregate sources and the control.

The fraction containing the highest measured organic-carbon concentration was therefore also the fraction associated with the greatest alteration in early hydration kinetics. This correspondence does not establish organic carbon as the sole cause of the measured differences.

The greater specific surface area, mineralogical composition, soluble constituents, and other chemical characteristics of the material passing the No. 100 sieve may also have influenced the calorimetric response.

4.5.1. Cumulative Heat and Strength

Cumulative heat release was compared with mortar compressive strength to determine whether early hydration behavior could provide an accelerated indication of subsequent mechanical performance. Comparisons were first made between cumulative heat and compressive strength measured at corresponding ages of 3 and 7 days. Additional comparisons evaluated 28-day strength against cumulative heat measured at 3 and 7 days to determine whether early calorimetric response provided insight into later-age strength development.

The three-day measurement is of interest because it captures the principal period of early cement hydration while providing results substantially earlier than conventional 7- or 28-day strength testing. Although cumulative heat at 3 days did not exhibit a strong linear relationship with absolute compressive strength across the evaluated aggregate sources, the measurement remains useful for identifying deviations in hydration behavior, including retardation, suppression of heat evolution, or departures from a source-specific baseline. Its principal value therefore lies in rapid performance characterization rather than direct prediction of compressive strength.

The 7-day comparison provides a longer observation period but offers less advantage as an accelerated screening method. Accordingly, the three-day calorimetry response was considered the more practical basis for identifying potentially abnormal hydration behavior and determining whether additional performance testing was warranted. The relationships between cumulative heat and contemporaneous mortar strength at 3 and 7 days are presented in Figure 4-20 and Figure 4-21.

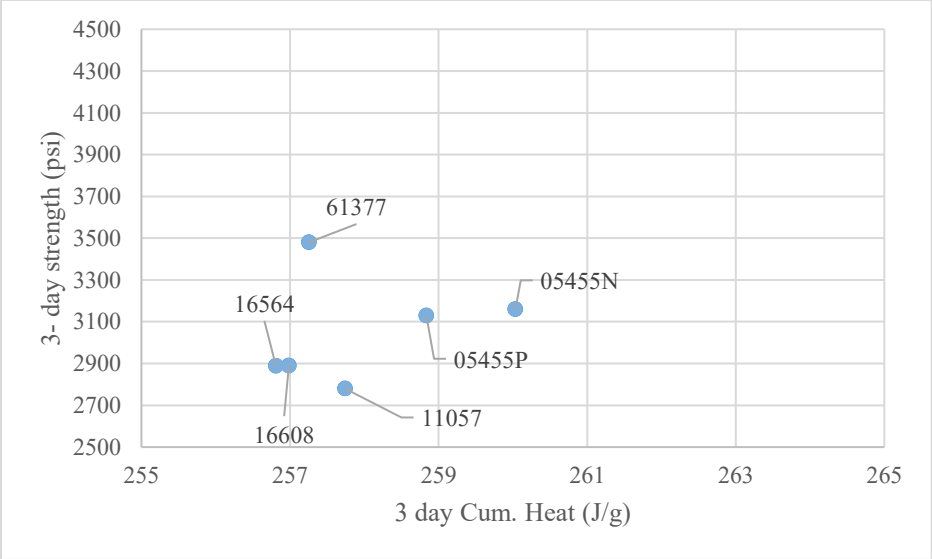

Figure 4-20: 3-Day Compressive Strength vs. 3-Day Cumulative Heat

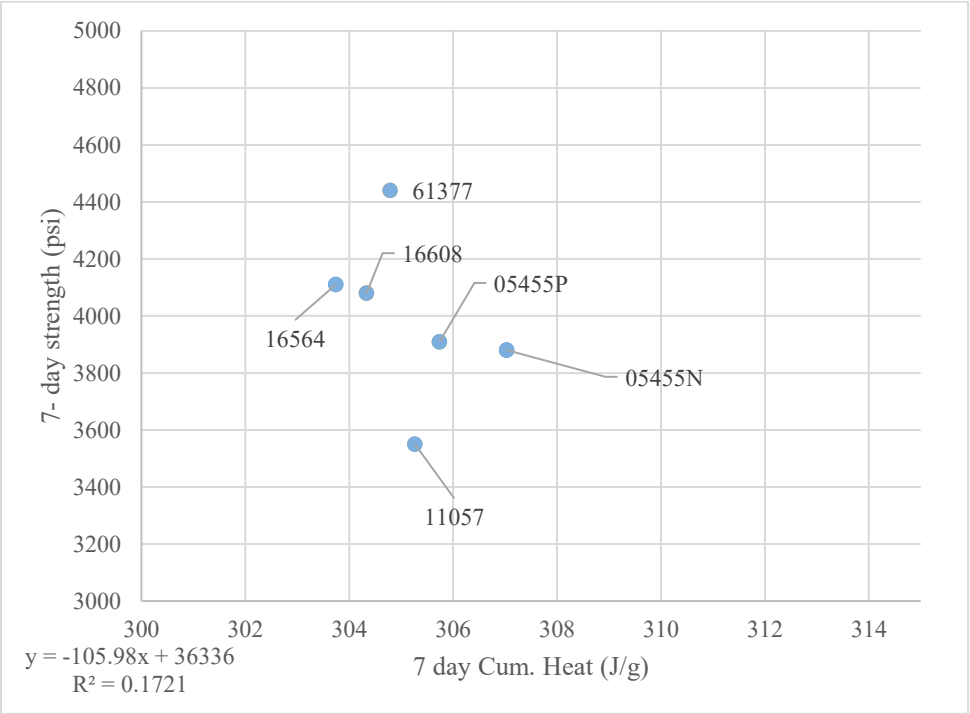

Figure 4-21: 7-Day Compressive Strength vs. 7-Day Cumulative Heat

The relationships between cumulative heat release and compressive strength were evaluated to determine whether calorimetry could predict mortar strength across the aggregate sources examined. No statistically meaningful relationship was identified at 3, 7, or 28 days. The coefficients of determination remained low at each age, indicating that differences in cumulative heat accounted for only a small portion of the observed variation in compressive strength. Although limited trends were apparent at the earlier ages, cumulative heat did not provide a reliable basis for predicting absolute strength across different aggregate sources.

The absence of a statewide relationship does not diminish the value of isothermal conduction calorimetry as a source-specific monitoring method. Cumulative heat measurements were comparatively consistent among the evaluated sands, while compressive-strength results exhibited substantially greater source-to-source variability. Once a representative hydration baseline and expected range of variability have been established for an individual mine, three-day calorimetry can provide a rapid means of identifying departures from normal production. A measurable reduction in cumulative heat, delay in peak occurrence, or suppression of heat flow relative to the source-specific baseline may indicate a change in aggregate characteristics that warrants additional evaluation. Calorimetry should therefore be interpreted as a sensitive comparative measure of changes within a source, rather than as a universal predictor of compressive strength among different mines.

4.5.2. Cumulative Heat and MWB

Cumulative heat release was evaluated against organic carbon measured with the modified Walkley–Black method to determine whether increasing organic-carbon content was associated

with measurable suppression of cement hydration. Because organic compounds can delay or inhibit early hydration reactions. The three-day response was of particular interest as a potential accelerated indicator of deleterious behavior shown in Figure 4-22.

The aggregate-wide regression obscures the most consequential source-specific response. Mine 11057, which presented the greatest concern in the mortar-strength evaluation, also exhibited the lowest three-day cumulative heat when its No. 100 sieve fraction was tested. This fraction contained among the highest concentrations of organic carbon measured with the modified Walkley–Black method, and its three-day cumulative heat was markedly lower than that of the bulk sands and the corresponding No. 100 fraction from mine 16608. The result provides evidence of a measurable early-age hydration effect associated with the fine fraction of mine 11057.

The response was not governed by organic-carbon concentration alone. Although the No. 100 fractions from mines 11057 and 16608 both contained elevated organic carbon, only the 11057 fraction exhibited pronounced suppression of three-day cumulative heat. This distinction indicates that the influence of organic matter depends on its chemical character, solubility, and interaction with cement hydration, rather than solely on the total quantity of oxidizable organic carbon present.

By seven days, the cumulative-heat values had largely converged, indicating that the early suppression observed for mine 11057 represented delayed hydration rather than a sustained reduction in the overall degree of reaction as shown in Figure 4-23. Accordingly, the principal significance of the three-day calorimetry result lies in its ability to identify an abnormal early hydration response that was not evident from the broader regression analysis. The 11057 results support the use of three-day isothermal calorimetry as a source-specific diagnostic tool, particularly when fine fractions exhibit elevated organic-carbon contents or when prior strength testing has identified performance concerns.

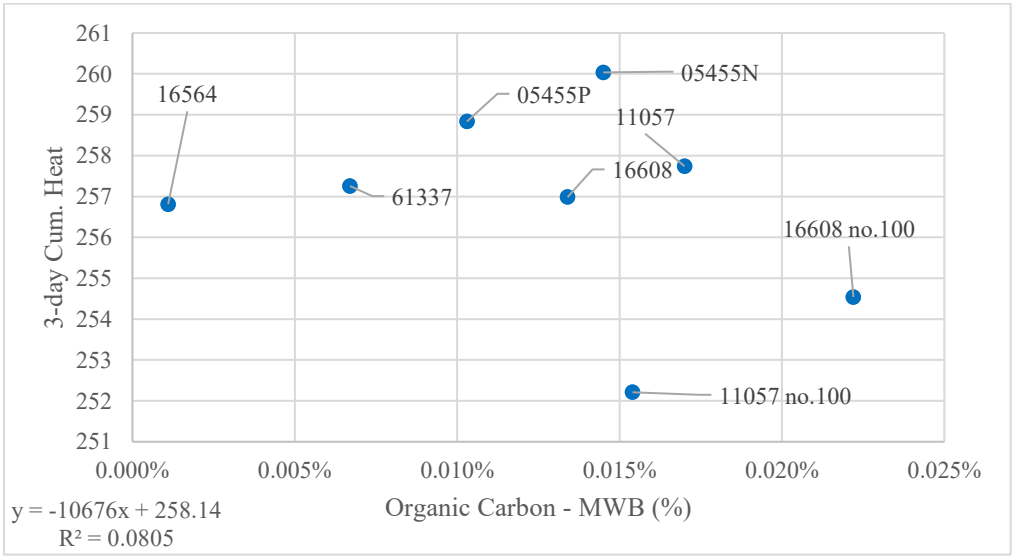

Figure 4-22: 3-Day Cumulative Heat vs. Organic Carbon (MWB)

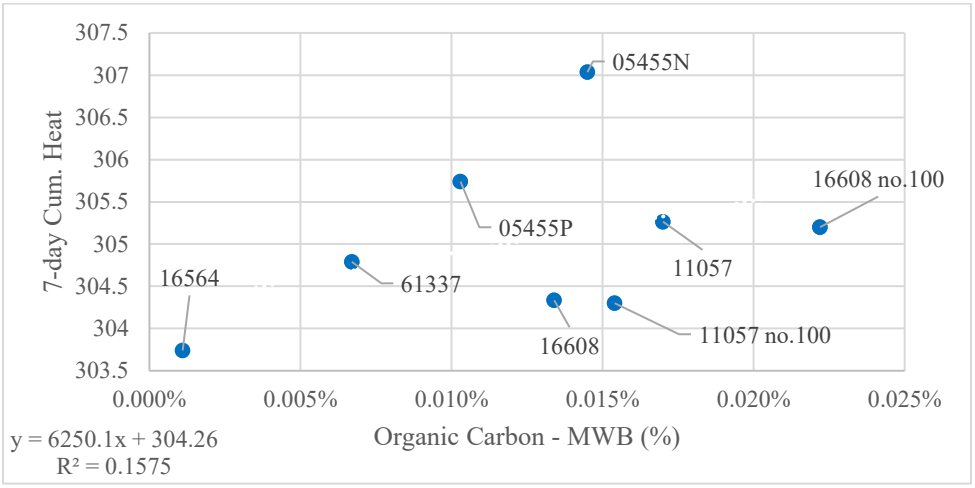

Figure 4-23: 7-Day Cumulative Heat vs. Organic Carbon (MWB)

4.5.3. Isothermal Conduction Calorimetry, Organic Carbon Testing and pH

Isothermal conduction calorimetry provides a highly sensitive measure of the rate and extent of cement hydration by continuously recording heat evolution under controlled temperature conditions. Because the method resolves changes in hydration kinetics over time, it can detect comparatively small alterations in the induction period, the onset of accelerated hydration, the magnitude of the principal silicate peak, and cumulative heat release. This sensitivity makes calorimetry particularly useful for identifying chemical or physical interactions that may not yet be evident from compressive-strength measurements alone. The method does not, however, independently establish the cause of an observed change. Variations in fines content, particle surface area, soluble constituents, mineralogy, and organic compounds may each alter the measured heat-flow curve.

The magnitude of the principal silicate hydration peak represents the maximum rate of heat evolution during accelerated hydration of the principal silicate phases in portland cement. A reduction in peak magnitude may indicate suppression of the hydration rate, although the interpretation must account for the aggregate fraction and other source-specific characteristics present in the system.

The relationship between organic carbon measured with the modified Walkley–Black method and the magnitude of the principal silicate hydration peak is presented in Figure 4-24. The coefficient of determination was 0.3699, indicating that organic-carbon content explained only a limited portion of the variation in maximum heat-flow rate. Although the fitted relationship decreased with increasing organic carbon, the natural fine aggregate sources generally produced peak magnitudes within a comparatively narrow range.

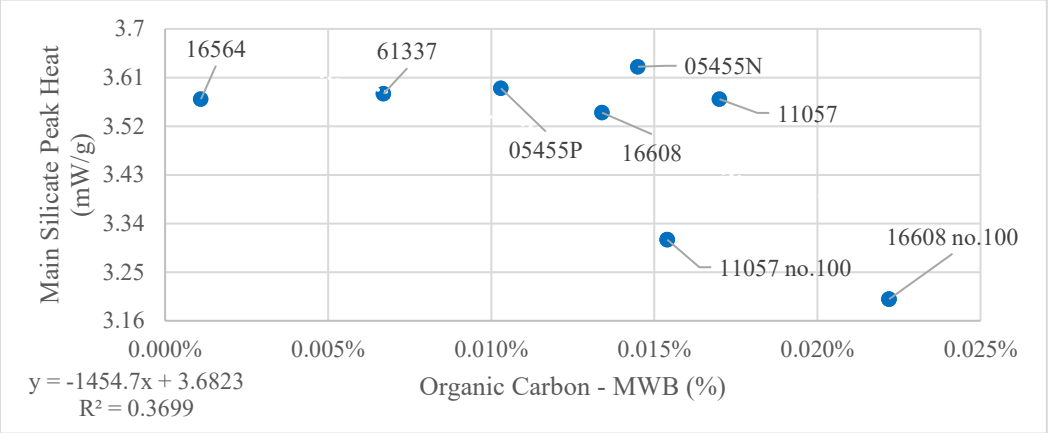

Figure 4-24: Main Silicate Peak Magnitude vs. Organic Carbon (MWB)

Mine 11057 produced a relatively low principal silicate peak compared with the other natural aggregate sources and also contained one of the higher measured organic-carbon contents. The result is consistent with a reduction in the maximum rate of silicate hydration, but it does not establish organic carbon as the controlling variable. Aggregate sources with lower organic-carbon contents produced both higher and comparable peak magnitudes, confirming that the measured differences were not governed by organic-carbon content alone.

The isolated No. 100 fractions from mines 11057 and 16608 produced substantially lower principal silicate peaks than the corresponding natural fine aggregates. These data exerted considerable influence on the fitted relationship and indicate that the fine fraction altered hydration more strongly than the measured organic-carbon concentration alone would suggest. The peak-magnitude results therefore identify source- and fraction-specific changes in silicate hydration but do not support a universal relationship between organic-carbon content and hydration suppression. reaction.

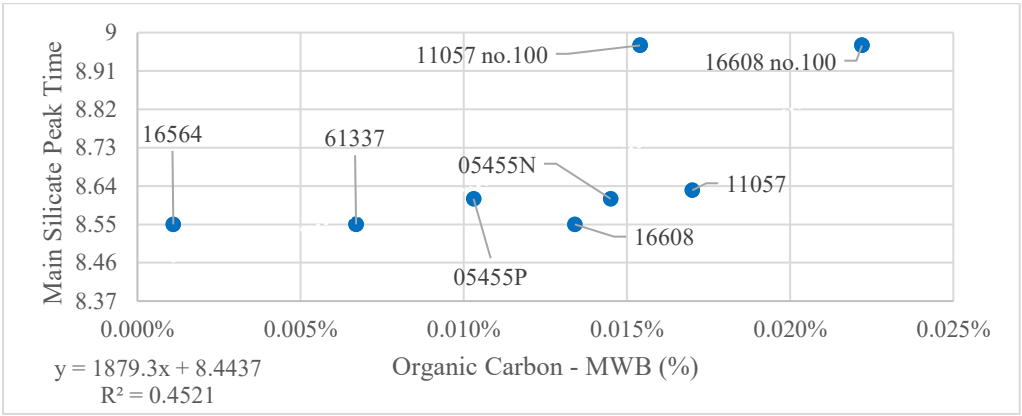

Figure 4-25: Main Silicate Peak Time vs. Organic Carbon (MWB)

Higher organic-carbon contents were generally associated with lower peak magnitudes and later peak occurrence. This response was most pronounced for the isolated No. 100 sieve fractions from mines 11057 and 16608, which contained the highest measured organic-carbon contents

and exhibited both the lowest peak magnitudes and the longest delays in peak occurrence. The concurrence of these responses is consistent with a reduction in the rate of early silicate hydration accompanied by an extension of the induction period.

The two parameters should not be interpreted as equivalent measures of retardation. A delayed peak indicates that the principal silicate reaction commenced later, but does not necessarily establish that the subsequent reaction proceeded at a substantially lower rate. Conversely, a reduction in peak magnitude indicates suppression of the maximum hydration rate, even where the timing of the peak remains comparatively unchanged. The simultaneous occurrence of a delayed peak and reduced peak magnitude therefore provides a more compelling indication of hydration interference than either response considered independently.

The bulk sand samples exhibited a comparatively narrow range of peak times and magnitudes, indicating that the naturally occurring organic contents of the as-received materials generally did not produce pronounced alterations in hydration kinetics. The apparent relationships across the complete dataset were not statistically significant and were influenced disproportionately by the isolated fine-fraction results. Accordingly, the data do not support a universal relationship between organic carbon measured with MWB and silicate-peak behavior across unrelated aggregate sources.

The relationships between sand pH and the principal calcium silicate hydration-peak characteristics are presented in Figure 4-26 and Figure 4-27. Neither peak magnitude nor peak timing exhibited a meaningful dependence on aggregate pH. The coefficients of determination were ($R^2 = 0.057$) for peak magnitude and ($R^2 = 0.003$) for peak time, indicating that variation in pH accounted for essentially none of the observed variation in hydration response. More importantly, both parameters remained confined to a narrow range across the evaluated natural fine aggregates. The limited variation in peak magnitude indicates that the maximum rate of silicate hydration was largely unaffected by differences in sand pH, while the similarly narrow range in peak timing demonstrates that the duration of the induction period and onset of accelerated hydration remained effectively unchanged. These results indicate that the hydration kinetics of the mortar systems were governed primarily by the cement, water content, and curing conditions rather than by the pH of the aggregate.

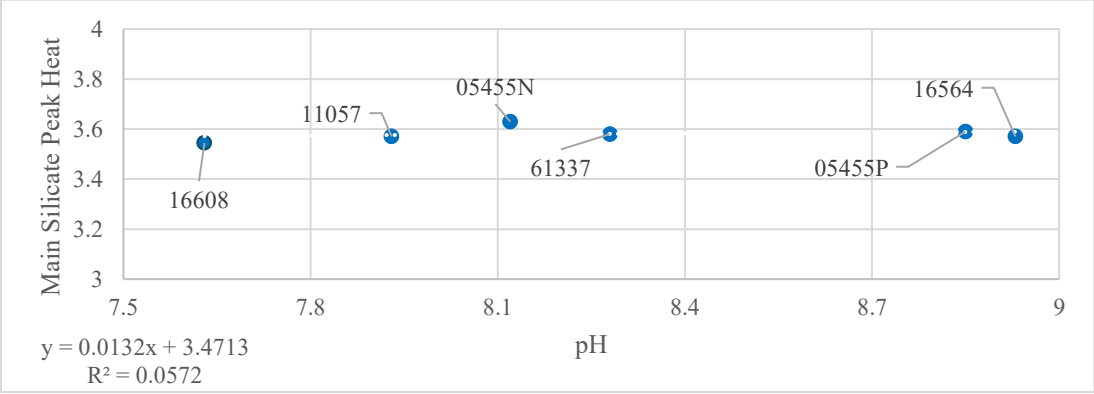

Figure 4-26: Main Silicate Peak Magnitude vs. pH

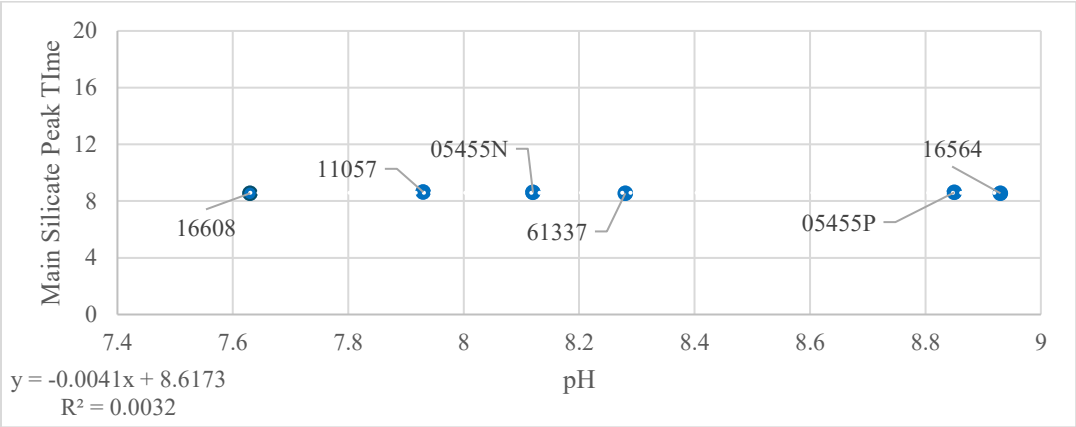

Figure 4-27: Main Silicate Peak Time vs. pH

Sand pH therefore provided little explanatory value for the observed calorimetric response. Within the range represented by the evaluated sources, aggregate pH did not measurably alter the rate or timing of the principal silicate reaction. Any source-specific effects associated with the sands were secondary to the intrinsic hydration behavior of the cementitious system and were not captured by pH alone.

4.6. Validation of the Modified Walkley–Black Method Using Known Carbon Additions

The modified Walkley–Black method was evaluated using controlled additions of two chemically distinct organic compounds, tannic acid and sucrose, to ASTM C778 standard graded sand. The experimental program was designed to determine whether the method could recover known quantities of organic carbon over a concentration range relevant to this investigation. Use of a standardized sand matrix minimized the mineralogical and compositional variability inherent to naturally mined sands, thereby allowing the analytical response to be attributed primarily to the introduced carbon source.

The evaluation was conducted in three stages:

- First, elemental analysis was used to determine the total carbon content of the tannic acid and sucrose. The measured carbon fractions, presented in Table 4-17, were then used to calculate the organic-carbon content of each dosed sand mixture.
- Second, ASTM C778 standard graded sand was dosed with each compound at replacement levels of 0.01%, 0.06%, 0.15%, and 0.30% by mass of sand. At each dosage, the organic compound replaced an equivalent mass of sand, thereby maintaining a constant total sample mass and providing a controlled addition of organic carbon to an otherwise uniform aggregate matrix.
- Third, each dosed sample was analyzed using the modified Walkley–Black method. The measured organic-carbon content was compared with the theoretical value calculated from the elemental-analysis results to evaluate carbon recovery, analytical bias, and the effective operating range of the procedure. Sample mass was adjusted, where required, to maintain the oxidation reaction within the measurable range of the method. This

controlled experimental design provided a direct assessment of the ability of the modified Walkley–Black method to detect and quantify known changes in organic-carbon content.

Table 4-17: Percent of Total Carbon Measured through Elemental Analysis

Organic Matter	Total Carbon (%)
Tannic Acid	48.76
Sucrose	43.00

Preliminary testing results showed 50-g sample mass exceeded the effective oxidation capacity of the modified Walkley–Black procedure using replacement levels of 0.06% and greater. At these concentrations, the organic carbon present in the dosed sands consumed the available potassium dichromate, preventing completion of the titration required for quantitative determination. The sample mass was therefore reduced progressively to maintain the oxidant demand within the working range of the method.

A 50-g sample was retained for the 0.01% replacement level. The sample mass was reduced to 25 g at 0.06%, 12.5 g at 0.15%, and 6.25 g at 0.30%. The same mass schedule was applied to both the tannic-acid- and sucrose-dosed sands to preserve consistency across the experimental matrix. These adjustments maintained an appropriate relationship between sample mass and oxidizable carbon content, thereby allowing the reaction and subsequent titration to proceed without exhausting the available oxidant. The sample masses used for each experimental condition are summarized in Table 4-18. condition.

Table 4-18: Mass of Sand Used for Modified Walkley-Black Test

ID	Mass of Sand Sample (g)
T-0.01	50
T-0.06	25
T-0.15	12.5
T-0.3	6.25
S-0.01	50
S-0.06	25
S-0.15	12.5
S-0.3	6.25

The comparison between expected organic-carbon content, calculated from elemental-analysis measurements, and organic carbon measured with the modified Walkley–Black method is presented in Table 4-19. Although the combined dataset exhibited a strong linear association ($R = 0.9922$), the agreement between expected and measured values varied substantially with concentration. The high correlation primarily reflects the ability of the method to preserve the ordering of samples across a broad concentration range; it does not establish equivalent analytical accuracy at each dosage.

Table 4-19: Modified Walkley-Black Organic Carbon Reading and Expected Reading According to Elemental Analyzer Results: Paired t-Test

ID	Expected % of Carbon (EA Estimate)	Actual % of Carbon (MWB)	Difference (Expected-Actual)
T-0.01	0.0049%	0.0091%	-0.0042%
T-0.06	0.0292%	0.0337%	-0.0045%
T-0.15	0.0731%	0.0680%	0.0051%
T-0.3	0.1462%	0.1380%	0.0082%
S-0.01	0.0042%	0.0080%	-0.0038%
S-0.06	0.0252%	0.0311%	-0.0059%
S-0.15	0.0630%	0.0703%	-0.0073%
S-0.3	0.1260%	0.1390%	-0.0130%
Mean	0.0590%	0.0622%	-0.0032%
	Standard Deviation		0.0068
	R		0.9922
	t-calculated		-1.324
	t-critical		2.365
	p (two tailed)		0.227

The greatest proportional discrepancy occurred at the 0.01% replacement level. For tannic acid, the expected carbon content was 0.0049%, whereas MWB measured 0.0091%, approximately 1.9 times the expected value. Similarly, the sucrose mixture had an expected carbon content of 0.0042% and an MWB result of 0.0080%, also approximately 1.9 times the expected value. As carbon content increased, the proportional differences generally diminished, and the measured values more closely approached the expected concentrations.

The paired t-test did not identify a statistically significant mean difference across the complete dataset where $t = -1.324$ and $p = 0.227$; however, this aggregate result masks the pronounced relative error at the lowest concentrations. The absence of a significant overall bias therefore should not be interpreted as evidence that the method provides adequate accuracy throughout its measurement range. Rather, the data indicate that MWB can distinguish broad changes in organic-carbon content at moderate dosages but lacks the precision required to resolve the very small differences encountered near the lower end of the tested range. This limitation is particularly important for the present investigation because the organic-carbon contents of many naturally mined sands fall within approximately 0.005% to 0.015%. Within this narrow concentration range, small absolute errors represent large proportional differences and reduce confidence in the method's ability to distinguish among closely spaced organic-carbon contents. The modified Walkley–Black method is therefore better suited to identifying broader differences in organic-carbon concentration than to resolving small variations near the lower end of its practical range.

Analytical characterization should consequently be supplemented with performance-based measurements capable of detecting whether constituents associated with the aggregate alter

cement hydration. Isothermal conduction calorimetry provides a more direct assessment of such interactions by resolving changes in hydration timing, peak development, and heat evolution that may not be apparent from organic-carbon concentration alone.

4.7. Evaluation of Mortar Cube Consolidation Procedures

Both AASHTO T 106 and ASTM C109 permit the use of qualified alternative consolidation procedures when the standard hand-tamping method is not employed. Because AASHTO T 71 relies on relatively small differences between the compressive strengths of mortars prepared with unwashed and washed sands, specimen-to-specimen variability can materially affect the interpretation of the resulting strength ratio. The consolidation study was therefore conducted to determine whether mechanical vibration could improve repeatability without introducing a systematic change in measured compressive strength.

Five natural fine aggregates were selected for the confirmatory evaluation. Mortar proportions were established in accordance with AASHTO T 71, with 600 g of portland cement and 360 g of water used for each mixture. The sand mass varied by source in accordance with the prescribed mixture proportions, while measured flow values ranged from 105.7% to 114.7%. The mixture quantities and corresponding flow results are summarized in Table 4-20.

Table 4-20: Mix Proportions Used for the Evaluation of Consolidation Techniques

Mine #	Sand (g)	IL Portland Cement (g)	Water (g)	Flow
16564	2150	600	360	106.6
16608	2050	600	360	107.8
11057	2190	600	360	105.7
61377	2137	600	360	110.5
05455N	1940	600	360	114.7

The evaluation was completed in two phases. The initial phase compared three consolidation procedures using mortar prepared in accordance with AASHTO T 106: standard hand tamping, low-energy vibration, and high-energy vibration. Two sets of three 50-mm cube specimens were prepared where the molds remained unrestrained during vibration and were permitted to move freely on the vibrating table in Mix 1. In the second mix (Mix 2), the molds were secured using the restraining device shown in Figure 4-28 to prevent translational movement during consolidation. Each cube received the same prescribed consolidation treatment within its respective group.

Figure 4-28: Restraining Device Used to Prevent Mold Movement During Vibrating Table Consolidation

The results demonstrate that consolidation method and mold restraint both influenced measured strength and repeatability. The unrestrained high-vibration condition produced the highest average compressive strength, but the associated variability remained comparatively high. By contrast, the restrained high-vibration condition produced the lowest coefficient of variation among the evaluated mechanical consolidation procedures. These findings indicate that restraint of the molds reduced variability introduced by uncontrolled mold movement and improved the consistency of mechanically consolidated specimens. The average strengths and coefficients of variation are presented in Figure 4-29 and Figure 4-30.

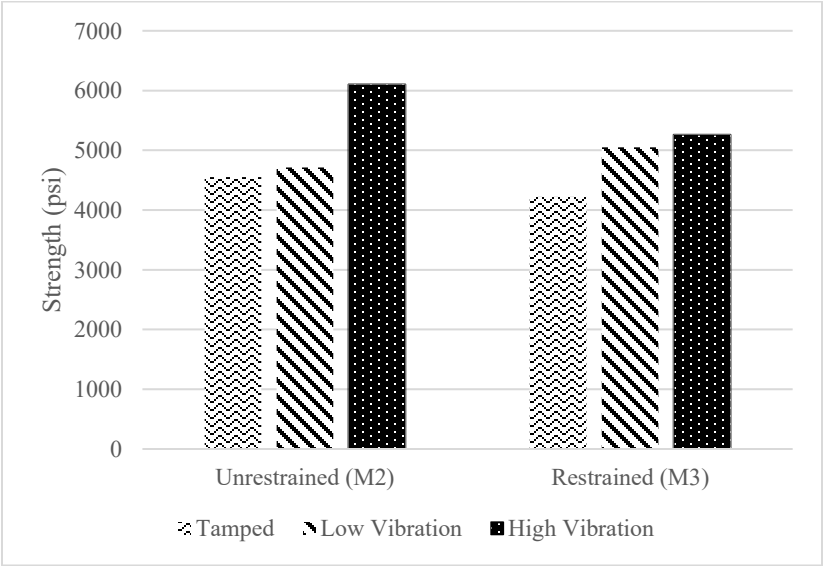

Figure 4-29: Compressive Strength of Mortar Cubes Consolidated Using Unrestrained and Restrained Conditions

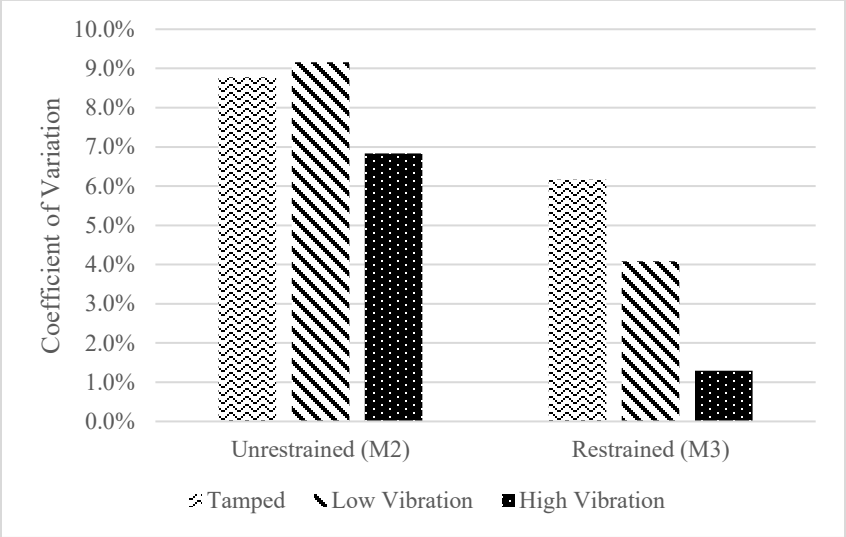

Figure 4-30: Coefficient of Variation of Compressive Strength of Mortar Cubes Consolidated Using Unrestrained and Restrained Conditions

The confirmatory phase compared standard hand tamping with restrained high-vibration consolidation using mortar prepared with five natural fine aggregates. Average compressive strength varied among aggregate sources and between consolidation procedures, but neither method produced consistently higher strengths across the complete dataset as shown in Figure 4-31. The influence of consolidation method was therefore source-dependent and could not be characterized as a uniform increase or reduction in measured strength.

Repeatability provided the more consequential basis for evaluating the two procedures. The standard hand-tamping method produced lower coefficients of variation for most of the aggregate sources, whereas restrained high-vibration consolidation resulted in substantially greater variability for several mixtures as shown in Figure 4-32. Although restrained vibration reduced the uncontrolled mold movement observed during the exploratory phase, mechanical vibration remained sensitive to mixture consistency, aggregate characteristics, and the distribution of consolidation energy within the specimens.

These findings are particularly important for AASHTO T 71, where aggregate qualification is based on the relative strength of mortars prepared with unwashed and washed sands. A consolidation procedure that introduces additional specimen variability can obscure the comparatively small strength differences used to determine compliance. Consequently, the standard hand-tamping procedure provided the more reliable basis for specimen fabrication and was retained for subsequent AASHTO T 71 testing. The restrained high-vibration procedure did not demonstrate sufficient improvement in either strength consistency or repeatability to support its adoption as an alternative consolidation method.

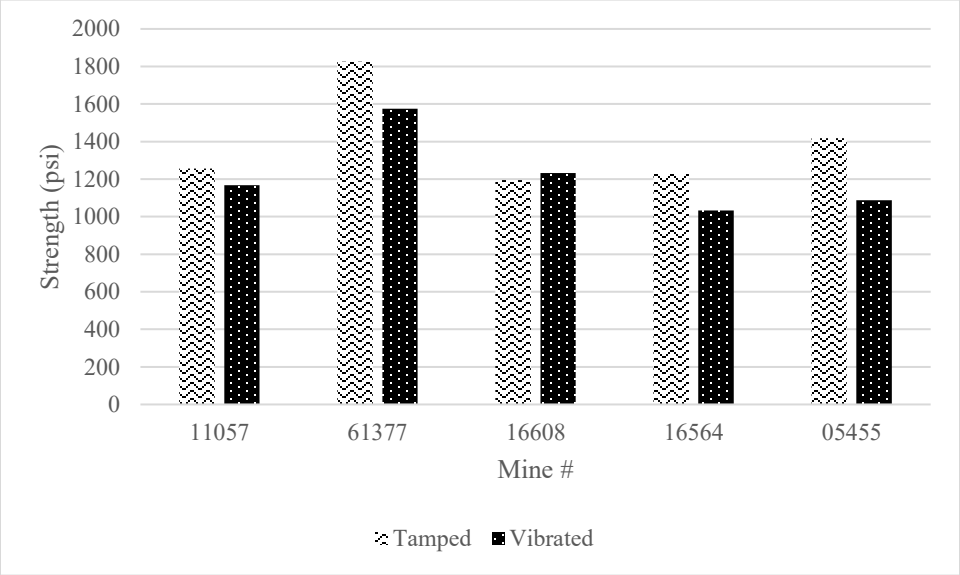

Figure 4-31: Comparison of Compressive Strength Results for Hand-Tamped and High-Vibration Consolidation Methods

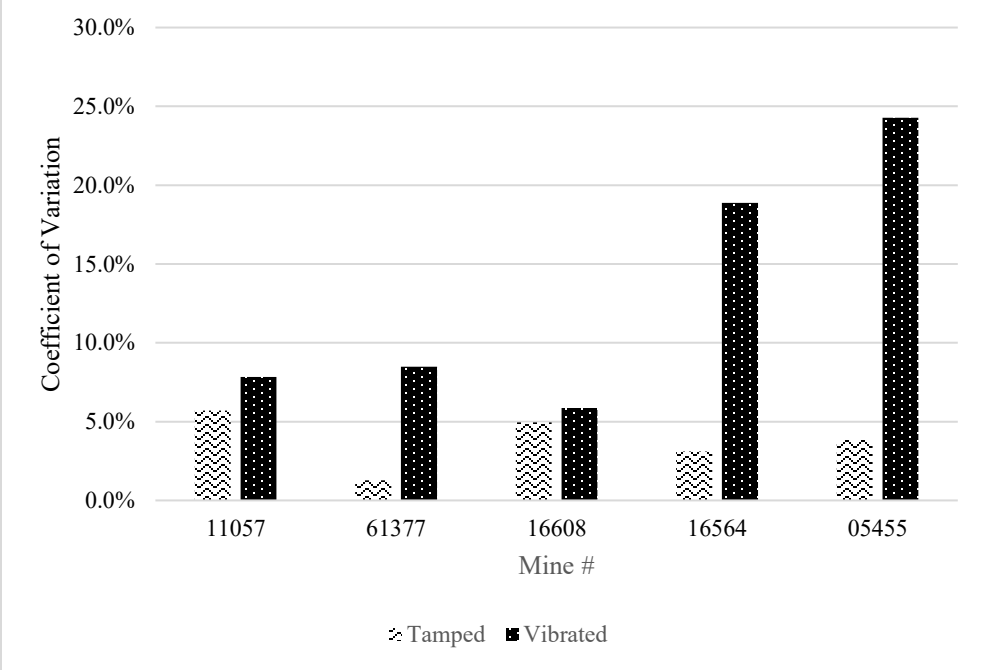

Figure 4-32: Coefficient of Variation of Compressive Strength Results for Hand-Tamped and High-Vibration Consolidation Methods

4.8. Organic-Acid-Dosed Sands Experiment

A controlled dosing program was conducted to isolate the effects of organic compound type and concentration from the inherent variability of naturally mined sands. ASTM C778 standard graded sand served as the reference aggregate, providing a uniform mineralogical and

gradational matrix with minimal naturally occurring organic matter. Selected organic compounds were introduced by replacing an equivalent mass of sand, thereby maintaining a constant total aggregate mass within each mixture.

4.8.1. AASHTO T 21

Color testing in accordance with AASHTO T 21 was performed on the ASTM C778 standard graded sand control and on sands containing controlled additions of humic acid, fulvic acid, tannic acid, and sucrose. The resulting organic plate classifications are summarized in Table 4-21, and the corresponding supernatant solutions are presented in Figure 4-33 - Figure 4-36.

Table 4-21: AASHTO T 21 Results on Controlled Additions of Organic Matter

ID	AASHTO T-21 Results
C-0	1
H-0.01	3*
H-0.06	5*
H-0.15	5*
H-0.3	Not Tested
F-0.01	1
F-0.06	3*
F-0.15	4*
F-0.3	Not Tested
T-0.01	2
T-0.06	4*
T-0.15	5*
T-0.3	Not Tested

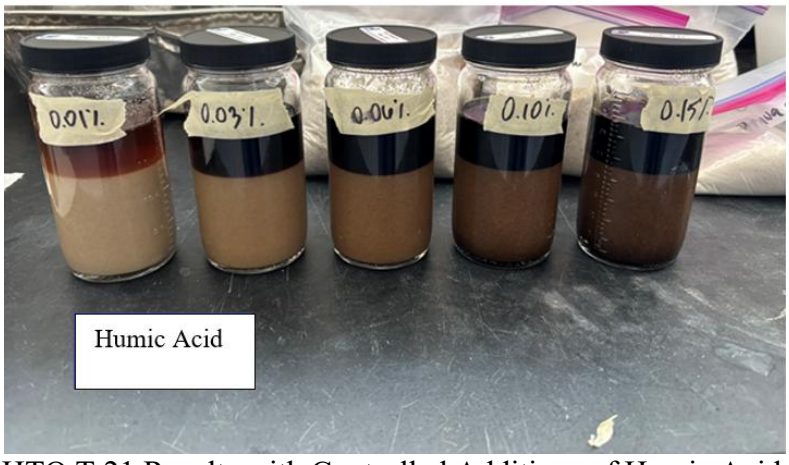

Figure 4-33: AASHTO T 21 Results with Controlled Additions of Humic Acid

Figure 4-34: AASHTO T 21 Results with Controlled Additions of Tannic Acid

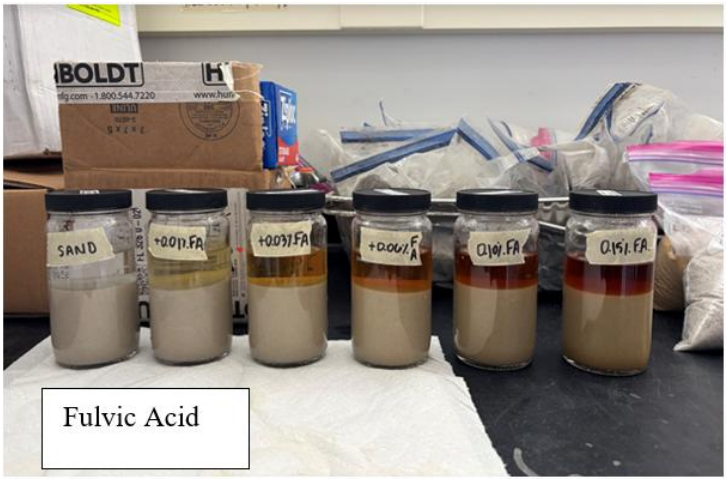

Figure 4-35: AASHTO T 21 Results with Controlled Additions of Fulvic Acid

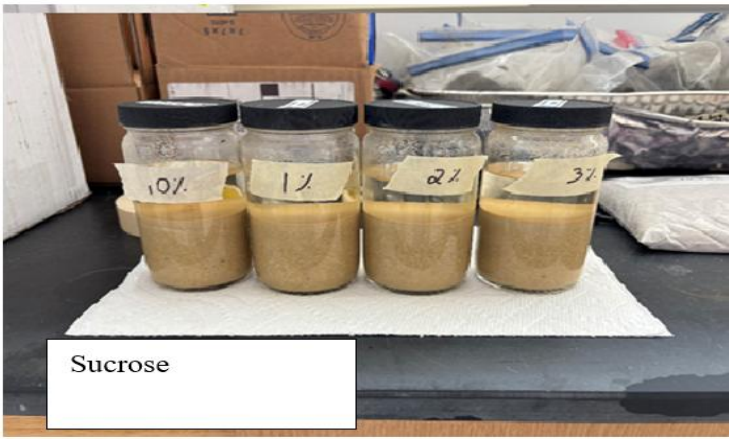

Figure 4-36: AASHTO T 21 Results with Controlled Additions of Sucrose

The control sand produced a minimal color response, confirming the suitability of the standardized aggregate as a reference material for the controlled dosing program. Progressive additions of humic, fulvic, and tannic acids generally produced darker supernatant solutions, although the onset and magnitude of color development differed among the compounds. The observed response therefore reflected more than organic concentration alone; chemical structure, alkaline solubility, and chromophoric character also governed the resulting plate classification.

Humic and fulvic acids produced the most pronounced color development at the higher replacement levels, consistent with the strongly colored, alkali-soluble character of humic substances. Tannic acid also exhibited a concentration-dependent response, but the progression differed from that observed for the humic compounds. These distinctions demonstrate that equal additions of different organic compounds do not produce equivalent AASHTO T 21 color responses.

Sucrose produced little or no visible color despite the introduction of organic carbon. This result is particularly consequential because sucrose can strongly retard cement hydration while remaining largely undetected by the colorimetric procedure. The absence of a dark supernatant therefore does not establish the absence of organic matter, nor does it preclude deleterious interaction with a cementitious system.

The controlled additions confirm that AASHTO T 21 is responsive to certain alkali-soluble, color-forming organic constituents, particularly at elevated concentrations. The method does not, however, provide a universal measure of organic content or a comprehensive indication of performance risk. Its proper function remains that of a selective qualitative screen whose interpretation depends on both the concentration and chemical character of the organic matter present.

4.8.2. Modified Walkley-Black and Elemental Analysis

Organic carbon was measured with the modified Walkley–Black method for each humic-acid, fulvic-acid-, and tannic-acid-dosed sand mixture. Triplicate measurements were performed at each replacement level, and the average values are summarized in Table 4-22. Sample mass was reduced progressively at the higher replacement levels to prevent exhaustion of the potassium dichromate and to maintain the oxidation reaction within the effective operating range of the method.

Table 4-22: Modified Walkley–Black Organic Carbon Results for Different Organic Acids and Levels of Replacement

Percent Replacement by Weight of Organic Matter	Organic Carbon - MWB (%)		
	Humic	Fulvic	Tannic
0.01%	0.0057%	0.0090%	0.0091%
0.06%	0.0198%	0.0335%	0.0337%
0.15%	0.0461%	0.0715%	0.0680%
0.30%	0.0951%	0.1570%	0.1380%

Organic carbon measured with the modified Walkley–Black method increased systematically with replacement level for each of the three organic compounds. The magnitude of the response differed among compounds, however, demonstrating that equal mass additions did not introduce equivalent quantities of carbon and did not produce identical analytical recoveries. At comparable replacement levels, fulvic and tannic acids generally yielded higher measured organic-carbon contents than humic acid.

Elemental analysis was used to establish the total carbon fraction of each organic compound. Tannic acid contained the highest total carbon content at 48.8%, followed by fulvic acid at 43.3% and humic acid at 37.1%, as summarized in Table 4-23. The modified Walkley–Black response did not reproduce this ordering. Regression slopes derived from the controlled dosing results corresponded to apparent carbon recoveries of approximately 30.9% for humic acid, 50.8% for fulvic acid, and 43.4% for tannic acid. MWB therefore underestimated the carbon associated with humic and tannic acids and overestimated the response associated with fulvic acid relative to elemental analysis.

Table 4-23: Carbon Content of the Organic Acids Determined by Elemental Analysis

Organic Matter	Total Carbon via via EA (%)	Organic Carbon – MWB (%)
Humic Acid	37.1	31
Fulvic Acid	43.3	51
Tannic Acid	48.8	43

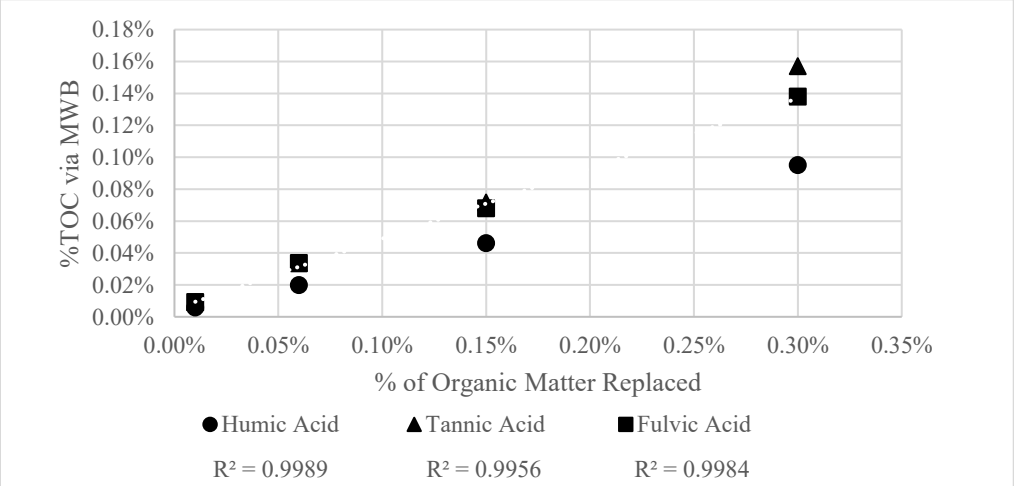

Figure 4-37: Relationship Between Organic Matter Replacement Level and Modified Walkley–Black Organic Carbon for Humic Acid, Fulvic Acid, and Tannic Acid

The relationship between organic-matter replacement level and organic carbon measured with MWB is presented in Figure 4-37. Strong linear relationships were observed for each compound, with coefficients of determination greater than 0.995. These results demonstrate that, under

controlled conditions and within the evaluated concentration range, the MWB method reliably tracked incremental changes in organic-carbon content. The method therefore distinguished both increasing dosage within a given compound and differences in carbon contribution among the three organic acids.

The observed linearity should not be interpreted as evidence that a single MWB response can be applied universally across different organic materials. The slope of the relationship varied with organic type because each compound contained a different carbon fraction and may have differed in oxidation efficiency under the MWB procedure. Consequently, the method is most defensible as a quantitative tool for monitoring relative changes within a defined material system or established source. It is less suitable for direct comparison among unrelated organic compounds unless their carbon content and analytical recovery have been independently characterized.

The distinction between MWB and AASHTO T 21 is also evident; where MWB produced a continuous quantitative response as organic dosage increased, whereas the AASHTO T 21 color classification depended strongly on the alkaline solubility and chromophoric character of the organic compound. The MWB is therefore better suited to tracking incremental changes in organic-carbon content, but the measurement does not independently establish whether the organic matter will impair cement hydration or mortar strength. An increase beyond a source-specific baseline should consequently trigger additional characterization or performance-based testing rather than serve as an independent basis for aggregate rejection.

4.8.3. pH Testing

Standardized laboratory testing was conducted to determine the pH response associated with the organic compounds used in the dosed-sand experiment. Duplicate measurements were obtained for each compound at every replacement level, and the average values are summarized in Table 4-24. The ASTM C778 standard graded sand control exhibited a pH of 6.04.

Table 4-24: pH Results for Different Organic Acids and Levels of Replacement

Percent Replacement by Weight of Organic Matter	pH		
	Humic	Fulvic	Tannic
0.01%	7.08	6.22	4.43
0.06%	8.8	5.71	3.63
0.15%	9.13	5.06	3.5
0.30%	9.28	4.81	3.19

Control pH was 6.04

The measured response depended strongly on organic type. Humic acid produced progressively more alkaline conditions as dosage increased, with pH rising from 7.08 at 0.01% replacement to 9.28 at 0.30%. Fulvic and tannic acids produced the opposite response. The pH of the fulvic-acid mixtures declined from 6.22 to 4.81 across the evaluated dosage range, while tannic acid produced the greatest acidification, decreasing from pH 4.43 to 3.19. These divergent trends

demonstrate that increasing organic-carbon content does not impose a uniform acid–base response on the sand-water system.

The relationship between organic carbon measured with the modified Walkley–Black method and pH is presented in Figure 4-38. Increased organic-carbon content corresponded to decreased pH for fulvic and tannic acids. Humic acid exhibited the inverse behavior, with pH increasing as organic-carbon content increased. The contrasting responses reflect differences in molecular structure, acidic functional groups, dissociation behavior, and buffering capacity among the compounds.

These results establish that pH and organic-carbon content describe distinct chemical attributes. The modified Walkley–Black method quantifies oxidizable organic carbon, whereas pH reflects the net acid–base equilibrium of the suspension. Interpretation of either measurement therefore requires consideration of the chemical identity of the organic matter present. Accordingly, pH should be treated as a supplemental descriptor of chemical condition rather than as an independent measure of organic content or a universal indicator of deleterious behavior. compound.

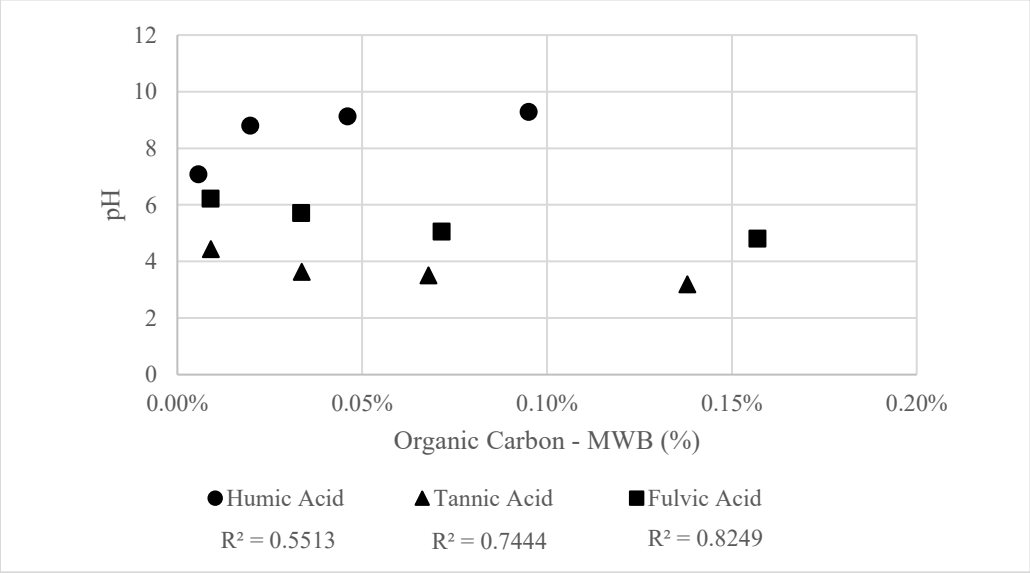

Figure 4-38: Relationship Between Modified Walkley–Black Organic Carbon and pH for Humic Acid, Fulvic Acid, and Tannic Acid

4.8.4. Organic Matter Effects on Cement Hydration and Mortar Strength

The controlled dosing program was used to determine how organic compound type and concentration influenced cement hydration kinetics and mortar strength development. Isothermal conduction calorimetry provided measurements of the timing and magnitude of the principal calcium silicate hydration peak and cumulative heat release, while compressive-strength testing quantified the corresponding mechanical response at 3, 7, and 28 days. The combined results are summarized in Table 4-25.

Interpretation of the data requires consideration of both hydration delay and the subsequent extent of reaction. A prolonged induction period indicates retardation of the principal silicate reaction, whereas a reduction in peak magnitude reflects suppression of the maximum hydration rate. Cumulative heat provides a broader measure of reaction progress but does not, by itself, establish the quality or spatial distribution of the resulting hydration products. Mortar strength may therefore diverge from calorimetric response where organic compounds alter microstructure, pore development, or the characteristics of the hydration products without proportionally reducing total heat release.

The following subsections evaluate humic acid, tannic acid, and fulvic acid individually before comparing the collective behavior of the three compounds. This structure allows compound-specific mechanisms to be distinguished from responses that were consistent across the broader experimental program

Table 4-25: Summary Result of Performance Testing on Controlled Additions of Different Types of Organic Matter to ASTM C778 Standard Graded Sand

Mine ID	Main Calcium Silicate Peak Power (mW/g)	Main Calcium Silicate Peak Time (h)	Cumulative Heat (J/g) @ 72 hours	Cumulative Heat (J/g) @ 168 hours	3-day strength (psi)	7-day strength (psi)	28-day strength (psi)
C-0	2.34	6.61	181.2	211.92	2450	3100	4330
H-0.01	2.29	6.97	179.12	209.57	1760	3430	4210
H-0.06	2.35	7.80	185.76	217.29	2180	2770	4250
H-0.15	2.44	10.53	199.84	236.78	2240	2810	4050
H-0.3	2.06	20.31	172.26	208.69	1500	2340	3150
F-0.01	2.34	7.1	181.78	212.86	1530	3430	4120
F-0.06	1.97	11.93	162.19	193.13	1500	1940	3150
F-0.15	1.93	30.86	150.91	201.1	0	1960	2760
F-0.3	0.99	105.5	19.42	155.82	0	660	980
T-0.01	2.14	15.05	175.92	210.77	2820	3430	3790
T-0.06	1.84	70.78	174.55	216.38	2390	3710	3800
T-0.15	1.42	151.76	61.69	209.77	300	3080	4340
T-0.3	ndp	ndp	21.255	33.75	0	0	0

ndp: non distinguishable peak was observed throughout the 7-day testing period.

4.8.4.1. Humic Acid

Humic acid produced a strongly dosage-dependent delay in the principal calcium silicate hydration reaction. The relationships between organic carbon measured with the modified Walkley–Black method and the normalized peak time and magnitude are presented in Figure 4-39 and Figure 4-40. Peak timing increased progressively with organic-carbon content, demonstrating a substantial extension of the induction period as humic-acid dosage increased. The principal silicate peak occurred at approximately 7 hours for the lowest replacement level and was delayed to nearly 20 hours at the highest dosage.

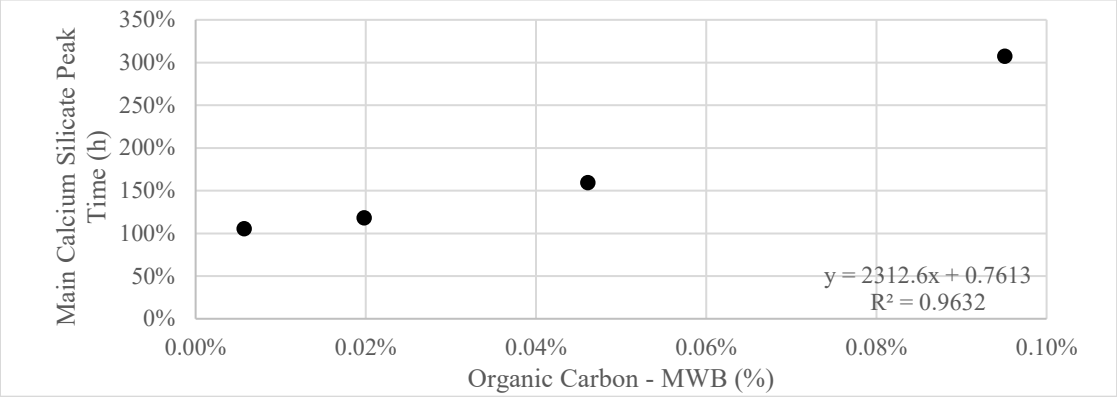

Figure 4-39: Normalized Time to Peak Power by Control vs. Organic Carbon for Humic Acid

The magnitude of the principal silicate peak exhibited a less uniform response. Intermediate replacement levels produced peak magnitudes comparable to or greater than the control, whereas the highest dosage produced a pronounced reduction. This distinction is important: delayed peak occurrence demonstrates retardation of the onset of accelerated hydration, but does not necessarily imply suppression of the reaction rate once the retardation barrier is overcome. The elevated peak magnitudes observed at intermediate dosages are consistent with renewed hydration following an extended induction period, during which reactive ions accumulated in the pore solution. At the highest dosage, however, the concurrent delay and reduction in peak magnitude indicate that the severity of the interference exceeded simple retardation and suppressed the subsequent silicate reaction. The retardation effect of humic acid is evident in Figure 4-39. As organic Carbon increased, the occurrence of the main silicate peak shifted progressively to later ages, increasing from approximately 7 hours at the lowest replacement level to nearly 20 hours at the highest replacement level. This trend is consistent with the mechanisms described in Section 3 and indicates that increasing humic acid concentrations systematically delay the hydration of the system.

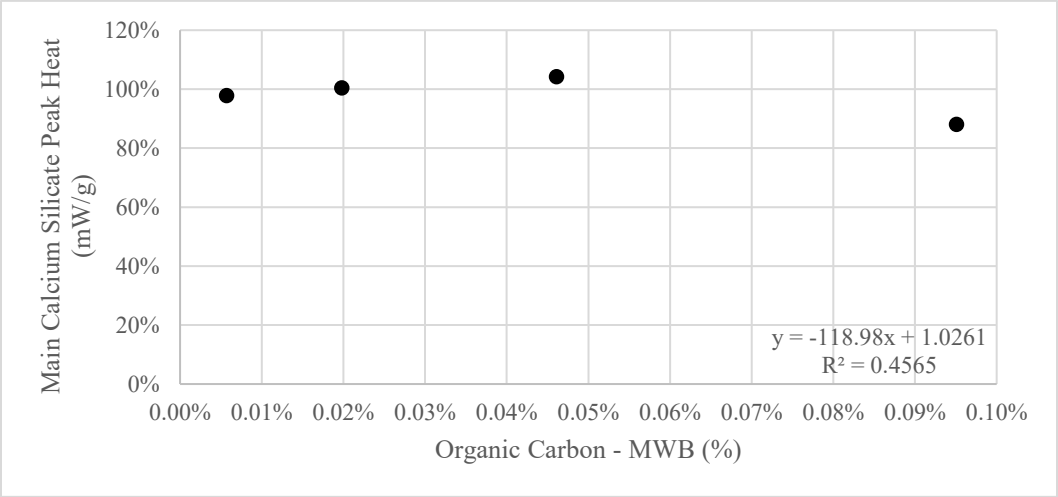

Figure 4-40: Normalized Magnitude of Peak Power vs. Organic Carbon for Humic Acid

The relationship between normalized cumulative heat release and mortar strength for the humic-acid mixtures is presented in Figure 4-41. Each measurement was normalized to the corresponding control value to permit direct comparison among replacement levels and testing ages. The horizontal reference line denotes the FDOT 95% strength criterion applied to the 7- and 28-day results.

At the intermediate replacement levels, H-0.06 and H-0.15, cumulative heat exceeded the control at both 3 and 7 days. These mixtures also developed strengths near or above the corresponding control values; however, the increase in strength was not proportional to the increase in cumulative heat. The calorimetric response indicates that hydration resumed vigorously after the extended induction period, but the additional heat release did not yield a commensurate mechanical benefit. Cumulative heat therefore reflects the overall extent of reaction without independently describing the efficiency with which the resulting hydration products contribute to strength development.

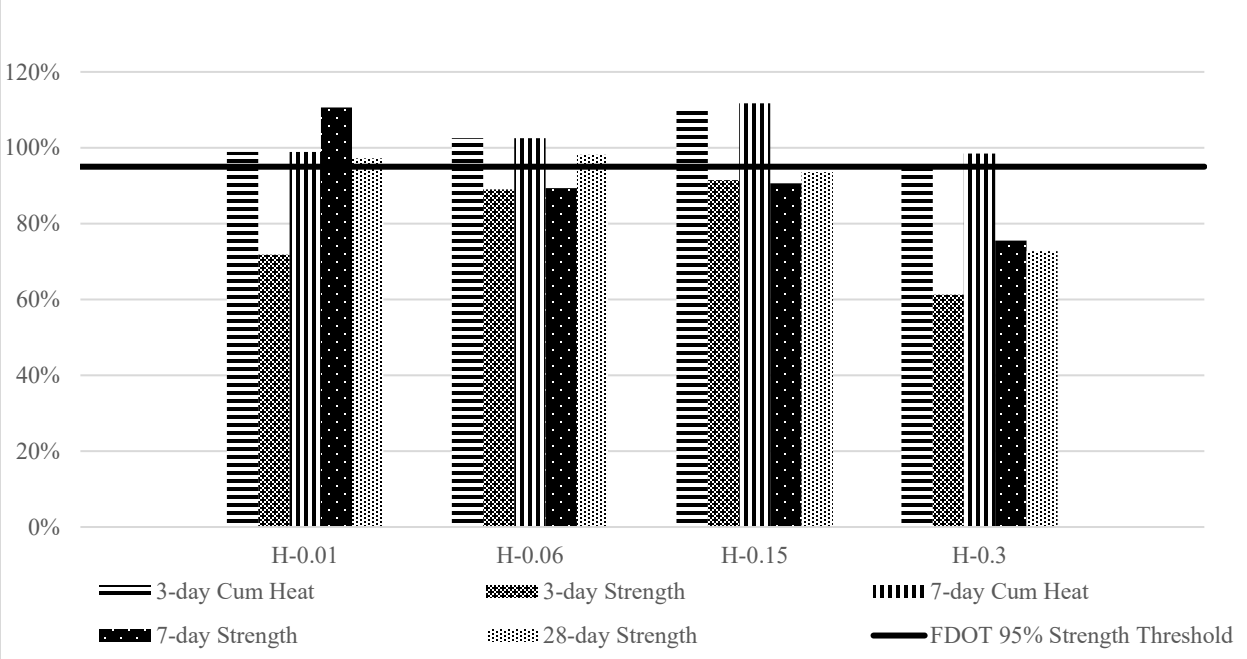

Figure 4-41: Normalized Strength and Heat Release for Each Replacement Level – Humic Acid

The lowest replacement level, H-0.01, exhibited a different response. Three-day cumulative heat remained near the control value, while the corresponding strength was substantially lower. By 7 days, strength had recovered and exceeded the control, even though cumulative heat remained approximately unchanged relative to the control. This behavior indicates that a near-normal degree of hydration can coexist with a pronounced early-age strength reduction and that subsequent strength recovery may occur without a corresponding increase in cumulative heat. The response is consistent with temporary disruption of early microstructural development rather than sustained suppression of the overall hydration reaction.

The highest replacement level, H-0.30, produced the most severe and persistent impairment. Cumulative heat and compressive strength were reduced at both 3 and 7 days, and the 28-day strength remained substantially below the control. Unlike the intermediate mixtures, H-0.30 did not recover sufficiently to satisfy the 95% strength criterion. The concurrence of an extended induction period, reduced peak magnitude, diminished cumulative heat release, and sustained strength loss indicates that the humic-acid concentration exceeded the level at which delayed hydration could subsequently compensate for the initial interference.

Taken collectively, the humic-acid results demonstrate that cumulative heat release did not provide a reliable quantitative prediction of strength. Peak timing furnished the clearest indication of increasing organic interference, whereas cumulative heat provided complementary information regarding the overall extent of reaction. The mechanical response depended not only on the quantity of hydration that occurred, but also on the timing of the reaction and the microstructural contribution of the resulting hydration products. A prolonged induction period therefore emerged as the most consistent calorimetric indicator of humic-acid dosage, while determination of strength performance continued to require direct mechanical testing.

4.8.4.2. Tannic Acid

Tannic acid produced a pronounced and systematically dosage-dependent influence on cement hydration. Increasing organic-carbon content was accompanied by a substantial extension of the induction period and a progressive reduction in the maximum rate of silicate hydration.

Peak timing provided the clearest indication of increasing interference. The principal calcium silicate peak occurred at approximately 15 hours for T-0.01, increased to nearly 70 hours for T-0.06, and was delayed to approximately 150 hours for T-0.15. At the highest replacement level, T-0.30, there was never a distinguishable main peak formed. This progression demonstrates that increasing tannic-acid concentration systematically delayed the onset of accelerated hydration, as presented in Figure 4-42 in a much more drastic way than humic acid.

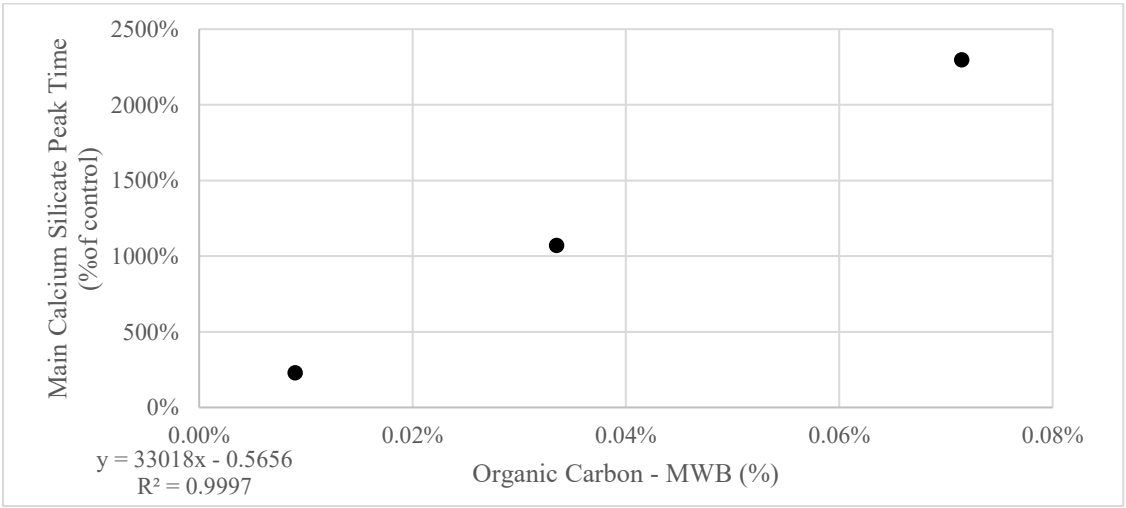

Figure 4-42: Normalized Time to Peak Power by Control vs. Organic Carbon for Tannic Acid

Peak magnitude of power declined concurrently with increasing dosage. Relative to the control, the principal silicate peak was moderately reduced at the two lowest replacement levels, substantially suppressed at T-0.15, and was nonexistent at T-0.30. The simultaneous delay in peak occurrence and reduction in peak magnitude provides compelling evidence that tannic acid affected both the initiation and intensity of the principal silicate reaction. At the lower replacement levels, hydration was delayed but ultimately resumed at an appreciable rate. At the highest dosage, the response progressed beyond retardation to near-complete suppression of hydration, as shown in Figure 4-43.

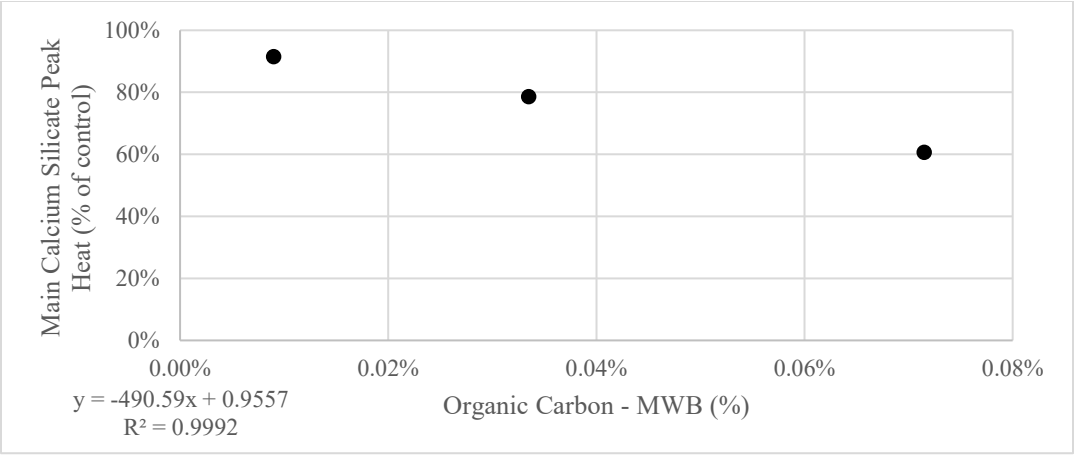

Figure 4-43: Normalized Magnitude of Peak Power vs. Organic Carbon for Tannic Acid

The cumulative-heat and mortar-strength responses for the tannic-acid mixtures are presented in Figure 4-44. T-0.01 and T-0.06 maintained cumulative heat values near those of the control through 7 days and developed comparable or greater early-age strengths; neither mixture, however, attained 95% of the control strength at 28 days. These results demonstrate that near-normal heat release and favorable early-age strength did not ensure equivalent later-age mechanical performance.

T-0.15 followed a markedly different progression. Three-day cumulative heat was reduced to approximately one-third of the control, and the corresponding strength represented only a small fraction of the control value. By 7 days, cumulative heat had recovered to nearly the control level and strength had increased substantially. At 28 days, the mixture developed strength essentially equivalent to the control. This recovery demonstrates that severe early retardation did not necessarily preclude later strength development when the principal hydration reaction ultimately resumed.

T-0.30 exhibited the most severe and persistent impairment. Cumulative heat remained substantially below the control at both 3 and 7 days, and no measurable compressive strength was obtained at any testing age. The elimination of peak magnitude, minimal cumulative heat release, and complete loss of strength indicates that the highest tannic-acid dosage effectively prevented normal hydration and mortar hardening.

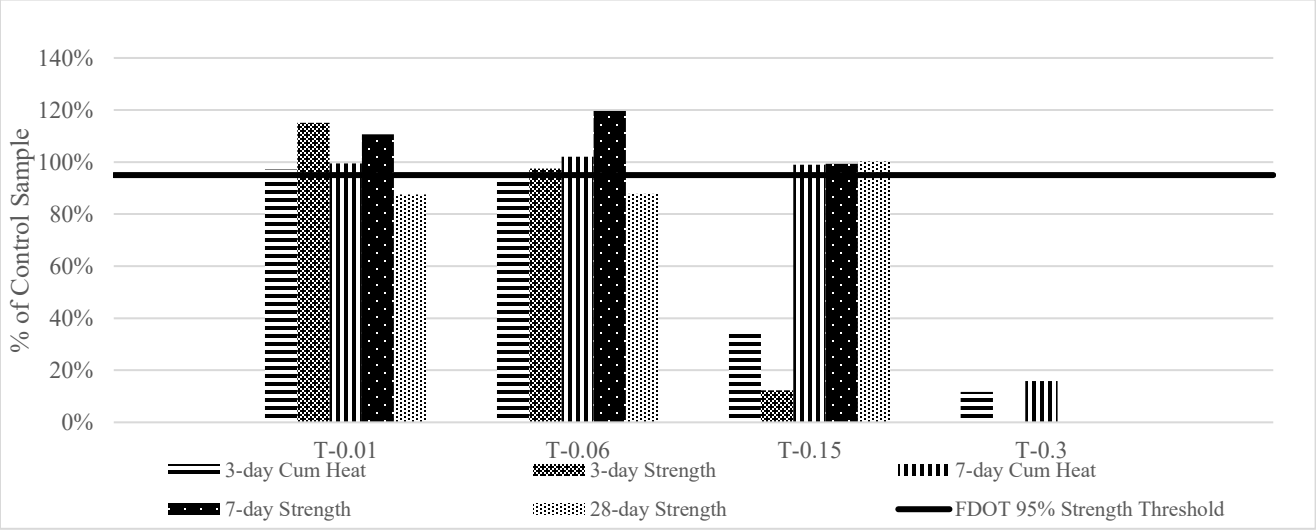

Figure 4-44: Normalized Strength and Heat Release for Each Replacement Level – Tannic Acid

Collectively, the tannic-acid results establish peak timing and peak magnitude as complementary indicators of organic interference. Peak timing quantified the progressive extension of the induction period, while peak magnitude reflected suppression of the maximum hydration rate. Cumulative heat documented the extent of subsequent reaction but did not independently predict later-age strength. Direct mechanical testing therefore remained necessary to determine whether resumed hydration ultimately produced satisfactory mortar performance.

4.8.4.3. Fulvic Acid

Fulvic acid produced a pronounced, dosage-dependent alteration of cement hydration, with increasing organic-carbon content associated with progressively delayed peak occurrence and reduced peak magnitude. The principal calcium silicate peak time increased from approximately 7 hours at the lowest replacement level to more than 100 hours at the highest dosage. The strength of this relationship, with a coefficient of determination of 0.948, demonstrates that peak timing provided a consistent measure of increasing fulvic-acid interference, as presented in Figure 4-45.

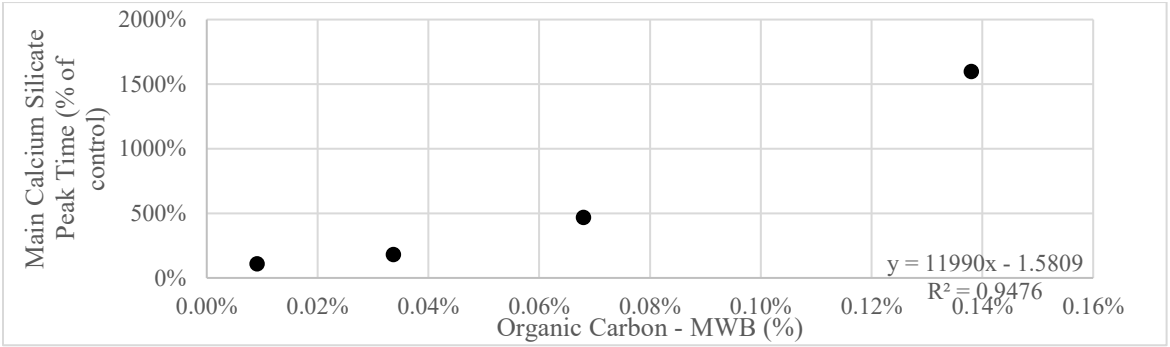

Figure 4-45: Normalized Time to Peak Power by Control vs. Organic Carbon for Fulvic Acid

Peak magnitude declined concurrently as organic-carbon content increased. The two lowest replacement levels retained comparatively high peak magnitudes, whereas the response decreased substantially at the intermediate and highest dosages. At F-0.30, the principal peak magnitude was reduced to approximately 40% of the control. The coefficient of determination of 0.949 indicates that increasing fulvic-acid concentration was closely associated with suppression of the maximum silicate hydration rate, as shown in Figure 4-46. The combined delay in peak occurrence and reduction in peak magnitude demonstrates that fulvic acid affected both the initiation and intensity of the principal hydration reaction.

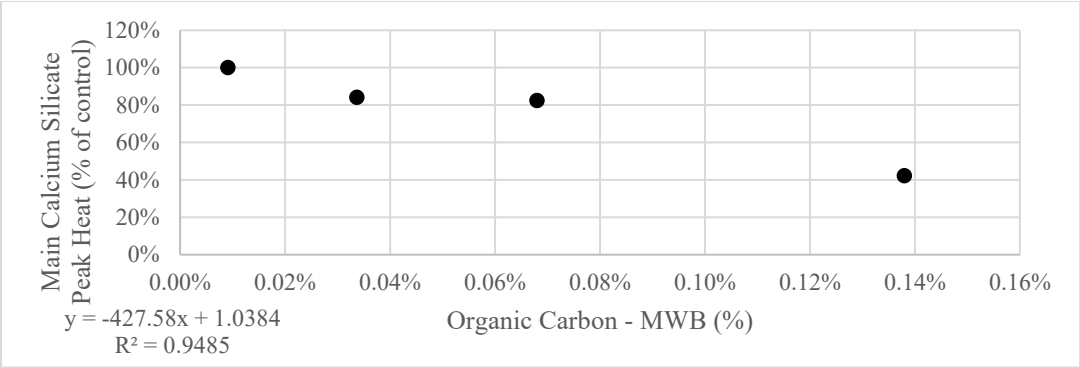

Figure 4-46: Normalized Magnitude of Peak Power vs. Organic Carbon for Fulvic Acid

The normalized cumulative-heat and mortar-strength responses for the fulvic-acid mixtures are presented in Figure 4-47. At the lowest replacement level, F-0.01, cumulative heat remained near the control throughout the evaluation period, yet three-day strength was substantially reduced. Strength recovered by 7 days and approached 95% of the control by 28 days. This response demonstrates that a near-normal degree of hydration did not preclude pronounced early-age mechanical impairment, although the effect was largely overcome with continued curing.

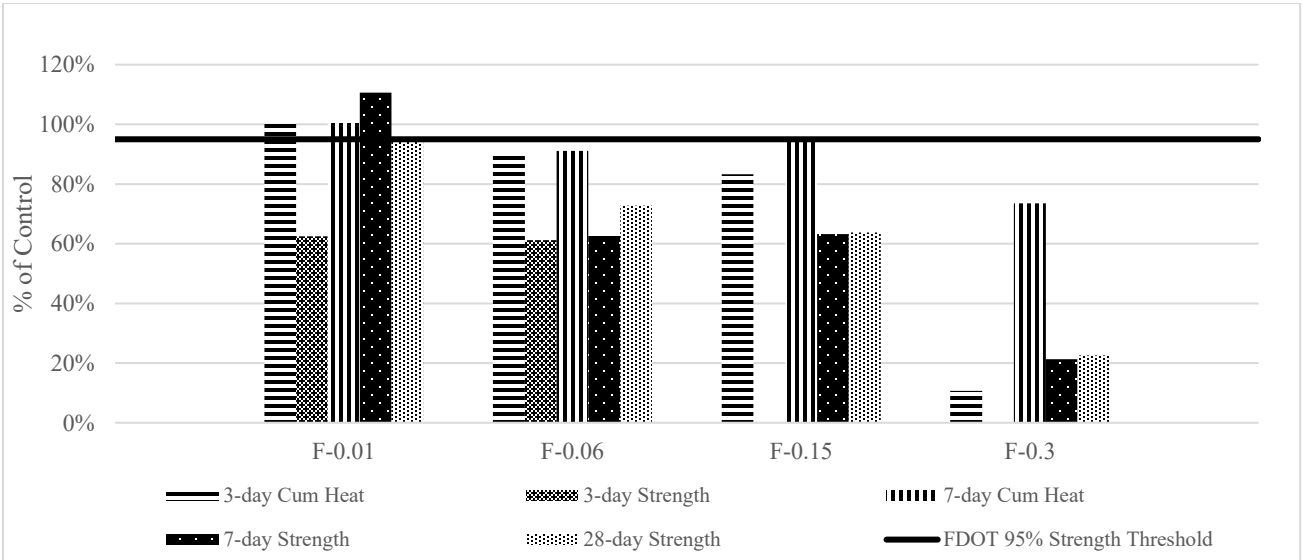

Figure 4-47: Normalized Strength and Heat Release for Each Replacement Level – Fulvic Acid

As more persistent divergence between hydration and strength occurred at the intermediate replacement levels. For F-0.06, cumulative heat recovered to approximately 90% of the control by 7 days, while strength remained near 60% and failed to recover to the 28-day acceptance threshold. F-0.15 exhibited an even more pronounced disparity. Despite three-day cumulative heat exceeding 80% of the control and seven-day cumulative heat approaching 95%, the mixture developed no measurable three-day strength, retained only approximately 60% of the control strength at 7 days, and remained substantially deficient at 28 days. The calorimetric recovery of these mixtures therefore overstated the extent of mechanical recovery.

F-0.30 exhibited the most severe impairment. Three-day cumulative heat was reduced to approximately 10% of the control, no measurable three-day strength was obtained, and strength remained severely depressed at the later testing ages. Cumulative heat increased to approximately 70% of the control by 7 days, but the corresponding strength remained near 20%. The partial resumption of hydration was therefore insufficient to restore meaningful mechanical performance.

The fulvic-acid results establish a clear distinction between the resumption of hydration and the development of load-bearing microstructure. Peak timing and peak magnitude responded systematically to increasing dosage and provided consistent indicators of hydration interference. Cumulative heat, by contrast, documented the extent of reaction without reliably characterizing the mechanical effectiveness of the products formed. The pronounced separation between heat release and strength at F-0.06 and F-0.15 suggests that fulvic acid altered not only hydration kinetics but also the quality, continuity, or spatial development of the resulting microstructure. Consequently, calorimetric recovery could not be interpreted as evidence of satisfactory strength recovery, and direct mechanical testing remained necessary.

Unlike the irregular strength patterns observed for humic and tannic acid, fulvic acid showed a more consistent trend: final strength decreased progressively with increasing replacement level, even as cumulative heat recovered across most levels by 7 days. In this case, organic Carbon proved a more reliable indicator of long-term strength loss than cumulative heat, suggesting that for fulvic acid the extent of organic content, rather than its effect on hydration kinetics, was the governing factor in mechanical performance. As with humic and tannic acid, the prolonged induction period remained the one consistent and reliable indicator across all replacement levels.

The three organic acids produced distinctly different strength development behaviors, despite having similar organic matter contents. Humic acid mixtures showed reduced early-age strength at all but the lowest replacement level; however, strength recovered over time, with low dosages approaching control values and higher replacement levels showing only modest reductions at 28 days. Tannic acid showed a complex and inconsistent response rather than a clear trend with dosage: the two lowest replacement levels exceeded the control at 7 days but fell below it at 28 days, whereas T-0.15 followed the opposite trend and achieved the highest strength, while T-0.30 effectively suppressed hydration. Fulvic acid produced the most severe impact, with strength remaining substantially reduced across all replacement levels, indicating a more harmful interaction with the cement system.

4.8.4.4. Integrated Evaluation of Organic Carbon and Hydration Parameters

The compound-specific evaluations demonstrated that humic, tannic, and fulvic acids altered cement hydration through distinct combinations of delayed peak development, reduced peak magnitude, and changes in strength development. The controlled-dosing results were subsequently combined to determine whether organic carbon provided a common quantitative basis for describing these changes across organic-matter types.

The combined dataset establishes a clear inverse relationship between organic carbon measured with the modified Walkley–Black method and the magnitude of the principal silicate hydration peak. The coefficient of determination was 0.753, indicating that increasing organic-carbon content accounted for a substantial portion of the reduction in maximum heat-flow rate across the evaluated organic compounds which is presented in Figure 4-48.

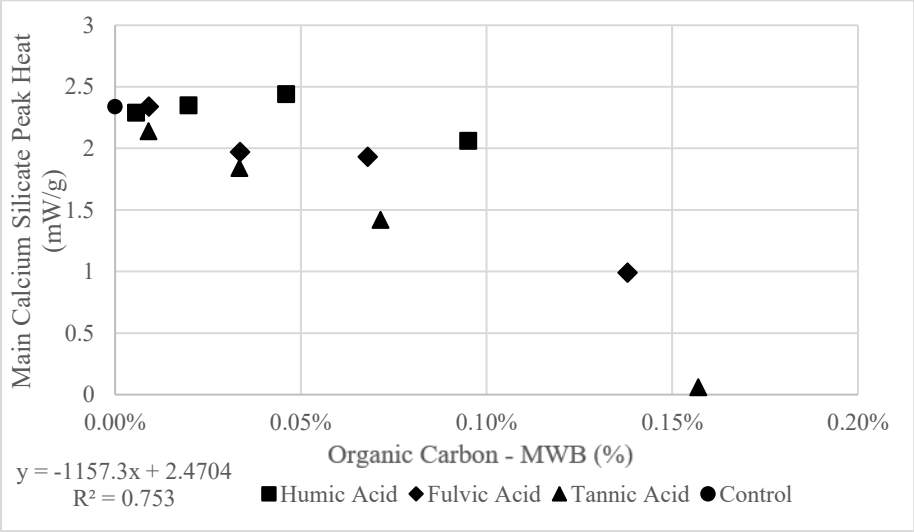

Figure 4-48: Main Hydration Peak Heat vs. Organic Carbon

The collective trend nevertheless conceals important differences among humic, fulvic, and tannic acids. Humic-acid additions retained comparatively high peak magnitudes over much of the evaluated concentration range, whereas fulvic and tannic acids produced progressively greater reductions as organic-carbon content increased. The highest tannic-acid dosage nearly eliminated the principal silicate peak, demonstrating that chemical identity governed the severity of hydration suppression even at comparable organic-carbon concentrations.

Organic-carbon content therefore provided a useful general descriptor of declining peak magnitude, but it did not fully account for the compound-specific differences in calorimetric behavior. The maximum rate of silicate hydration reflected both the concentration of organic carbon and the chemical character of the organic constituent introduced into the cementitious system.

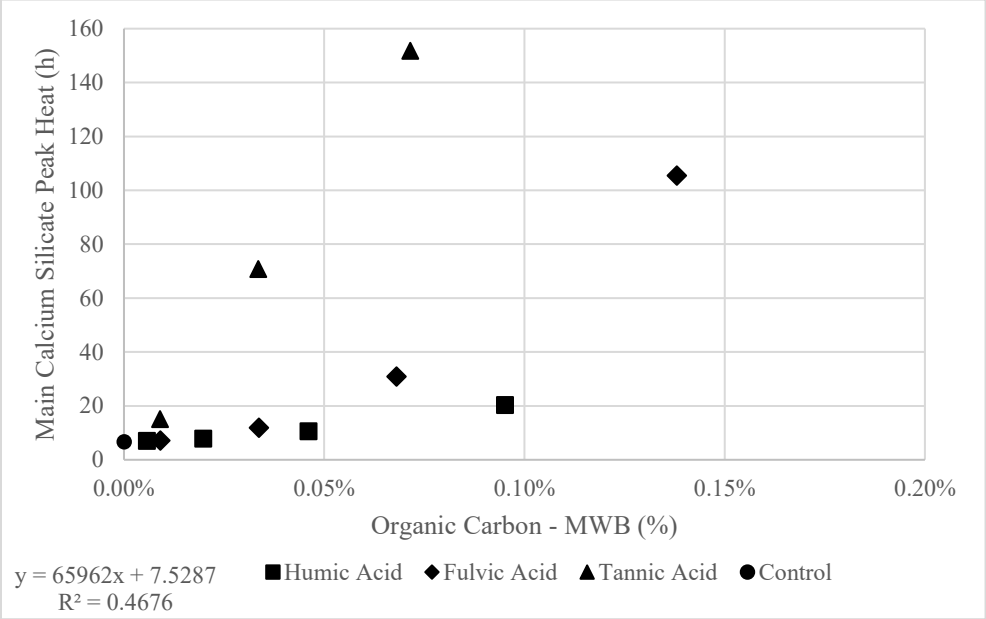

Figure 4-49: Time to Main Hydration Peak vs. Organic Carbon

The combined dataset demonstrated a general increase in the time required to reach the principal silicate hydration peak as organic-carbon content increased, consistent with hydration retardation. The coefficient of determination ($R^2 = 0.4676$) indicates that organic-carbon concentration explained a portion of the observed variation in peak timing, although the extent of retardation also depended on the specific organic compound. The relationship is presented in Figure 4-49.

The combined organic-acid dataset was evaluated to determine whether cumulative heat, AASHTO T 21 color response, or organic carbon measured with the modified Walkley–Black method provided a consistent basis for interpreting mortar compressive strength. The resulting relationships establish clear differences in the diagnostic value of the evaluated parameters.

Three-day cumulative heat exhibited a positive relationship with three-day compressive strength, with a coefficient of determination of 0.6629, as presented in Figure 4-50. Mixtures that released very little heat during the first three days generally failed to develop measurable strength, while mixtures approaching the cumulative heat of the control produced substantially greater strengths. The relationship was not proportional across the full dataset. Several mixtures with comparable cumulative heat developed markedly different strengths, indicating that the quantity of heat released did not independently define the efficiency with which hydration products contributed to load-bearing microstructure.

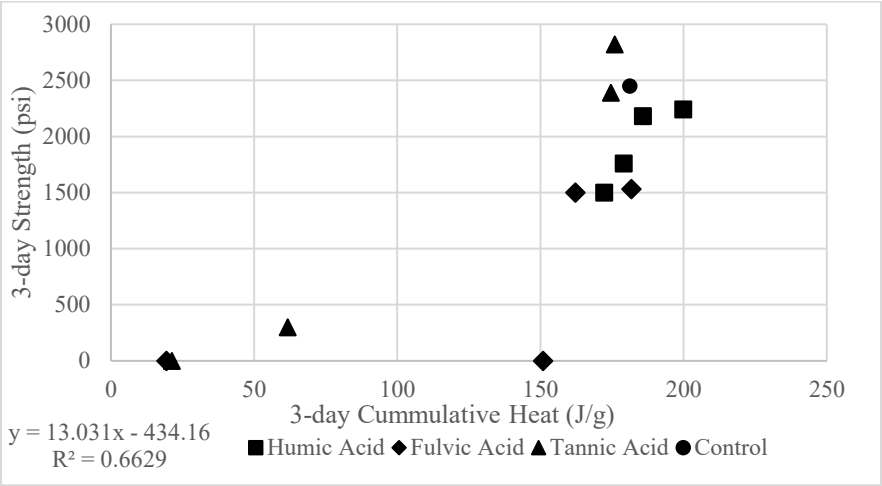

Figure 4-50: 3-Day Cumulative Heat vs. 3-Day Compressive Strength

The relationship between seven-day cumulative heat and seven-day compressive strength produced a coefficient of determination of 0.6966, as presented in Figure 4-51. Mixtures exhibiting the lowest cumulative heat also developed the lowest compressive strengths, whereas mixtures approaching the upper range of cumulative heat generally attained greater strength. The dispersion among mixtures with comparable heat release nevertheless remained substantial. Cumulative heat therefore provided a meaningful measure of hydration progression, but it did not independently define the extent to which the resulting hydration products contributed to load-bearing microstructure.

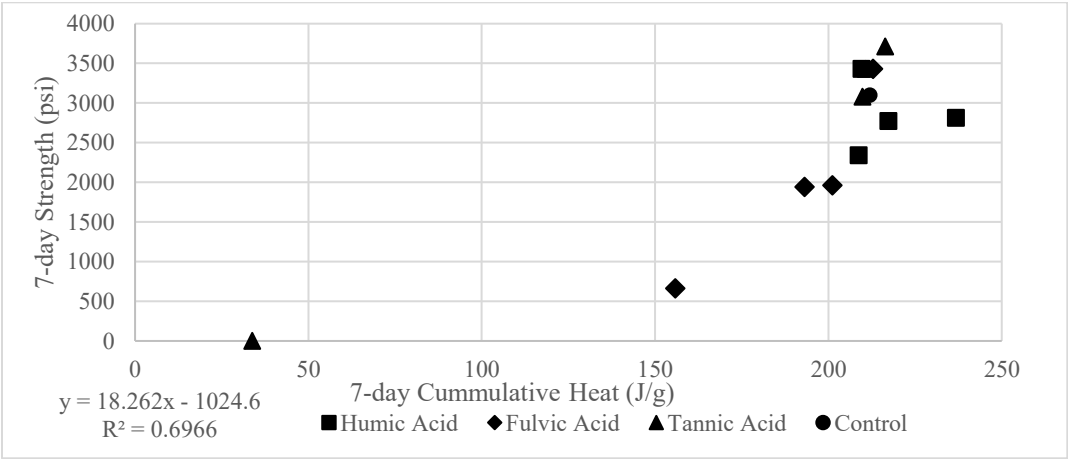

Figure 4-51: 7-Day Cumulative Heat vs. 7-Day Compressive Strength

The relationship between seven-day cumulative heat and 28-day compressive strength is presented in Figure 4-52. The coefficient of determination is 0.7976, indicating that the extent of hydration achieved within the first seven days accounted for a substantial portion of the variation in later-age strength. Mixtures exhibiting the lowest cumulative heat also developed the most severe reductions in 28-day compressive strength, including the tannic-acid mixture that produced essentially no measurable strength and the fulvic-acid mixture that remained near 1,000 psi.

Mixtures with seven-day cumulative heat above approximately 200 J/g generally developed substantially greater 28-day strengths, although several remained below the FDOT 95% threshold. This distinction demonstrates that recovery in cumulative heat did not necessarily correspond to full recovery in mechanical performance. The data therefore support seven-day cumulative heat as a meaningful indicator of later strength development, particularly for identifying mixtures subjected to severe and persistent hydration suppression. The remaining dispersion among mixtures with comparable heat release confirms that cumulative heat alone does not fully describe the quality, continuity, or load-bearing capacity of the hydration products formed.

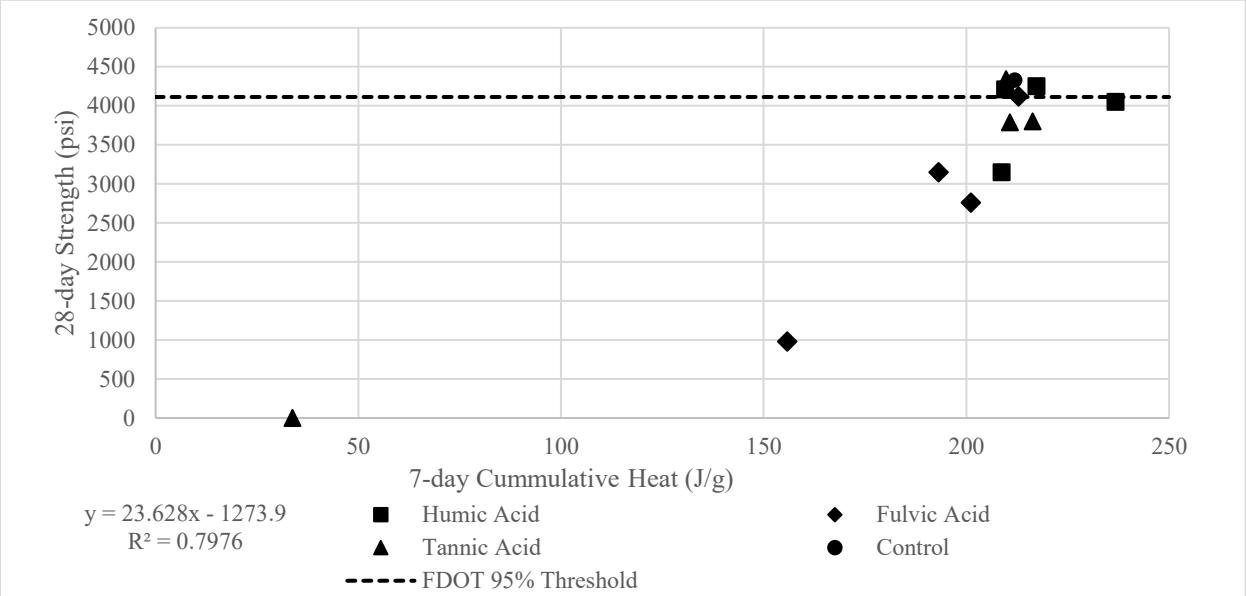

Figure 4-52: 7-Day Cumulative Heat vs. 28-Day Compressive Strength

The relationship between AASHTO T 21 plate number and 28-day mortar compressive strength is presented in Figure 4-53. The coefficient of determination was 0.1664, confirming that the color classification accounted for little of the variation in strength across the controlled organic-acid mixtures. Identical plate numbers encompassed markedly different mechanical outcomes. A plate number of 5, for example, included mixtures that developed strengths comparable with the control, mixtures that remained substantially below the FDOT 95% threshold, and mixtures that developed essentially no measurable strength.

The absence of a consistent strength gradient across the plate-number scale reflects the selective nature of the AASHTO T 21 procedure. The color response depends on the alkaline solubility and chromophoric characteristics of the organic compound rather than on its capacity to interfere with cement hydration or strength development. Tannic, fulvic, and humic acids therefore produced different combinations of color intensity and compressive-strength loss at comparable classifications.

The AASHTO T 21 color score consequently retained value as a qualitative indicator of alkali-soluble, color-forming organic matter, but it did not provide a quantitative measure of the

severity of strength reduction across chemically distinct organic compounds. Direct mortar performance testing remained necessary to determine whether a particular organic constituent produced an unacceptable reduction in 28-day compressive strength.

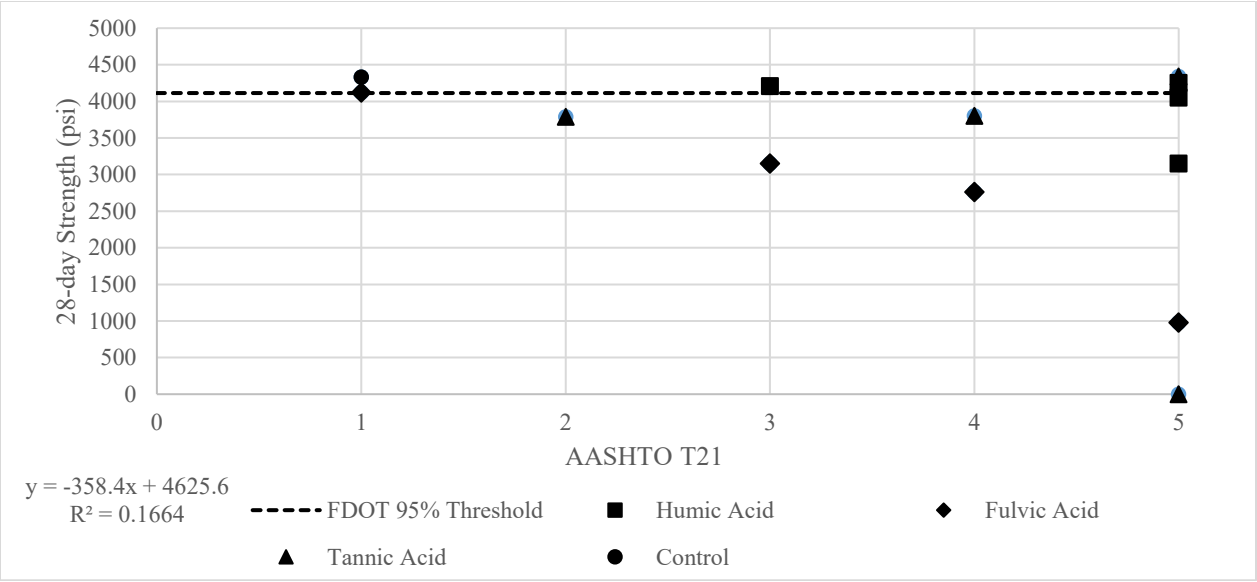

Figure 4-53: AASHTO T 21 Plate Number vs. 28-Day Compressive Strength

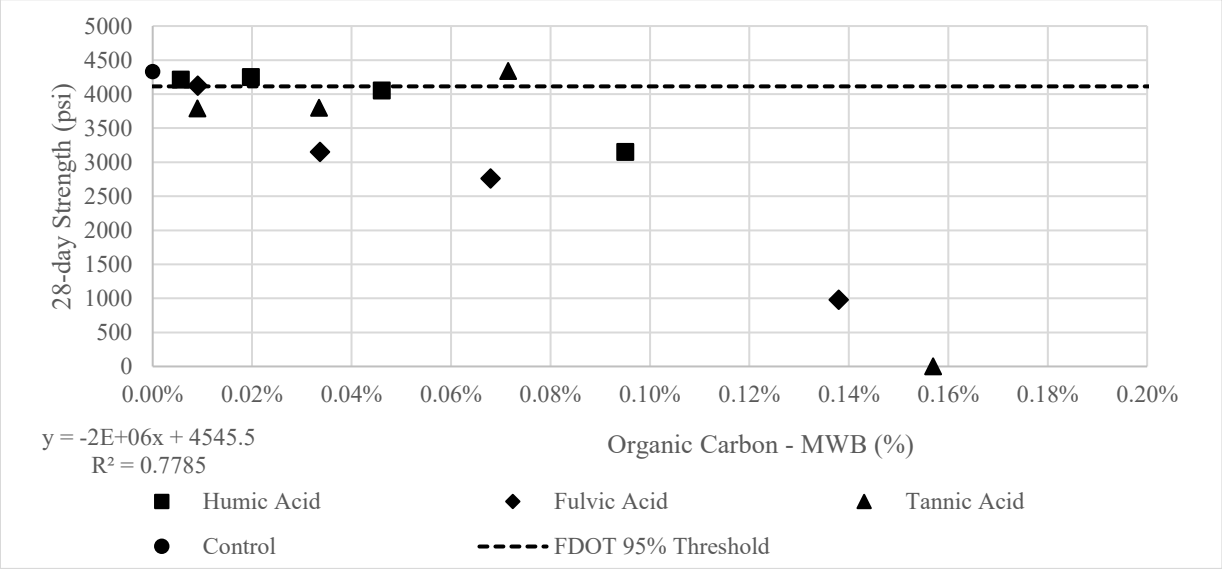

Figure 4-54: Organic Carbon vs. 28-Day Compressive Strength

The relationship between organic carbon measured with the modified Walkley–Black method and 28-day mortar compressive strength is presented in Figure 4-54. The combined dataset exhibited a strong inverse association, with a correlation coefficient of −0.882 and a coefficient of determination of 0.778. Increasing organic-carbon content was therefore accompanied by a pronounced reduction in 28-day strength across the controlled organic-acid additions.

The strength of the fitted relationship was influenced principally by the high-dosage mixtures, where the largest organic-carbon concentrations coincided with the most severe losses in compressive strength. The controlled additions extended well beyond the range measured in the naturally occurring aggregate sources, and the regression should therefore not be interpreted as a universal predictive equation for field materials.

Differences among humic, fulvic, and tannic acids further limit any direct interpretation based on organic-carbon concentration alone. Comparable organic-carbon contents produced different 28-day strengths, confirming that the chemical identity of the organic constituent governed the severity of its effect on cement hydration and strength development. The regression consequently represents the aggregate suppressive tendency observed across the complete experimental range rather than an invariant relationship applicable to organic compounds.

These differences highlight that organic matter type governs not only the severity but the nature of the effect on cement performance, and that the same organic Carbon level can produce markedly different outcomes depending on which organic compounds are present, a distinction that is practically unachievable to determine in field samples. What remains consistent across all three acids is that increasing organic Carbon produced a progressively longer induction period and, in most cases, a depression of the main calcium silicate peak. Strength did not follow a consistent trend, highlighting the complexity of predicting mechanical performance in the presence of organic matter. Elevated organic Carbon accompanied by a prolonged induction period and suppressed peak magnitude represents the most interpretable signal that organic matter poses a risk to cement performance. The implications of which on structural performance would require engineering judgment.

4.9. Integrated Interpretation and Implications for Aggregate Qualification

The principal results from the modified Walkley–Black analysis, isothermal conduction calorimetry, and AASHTO T 71 mortar testing are summarized Table 4-26. The combined evaluation was undertaken to determine whether measured organic-carbon content or early hydration characteristics provided a consistent explanation for the strength performance of the evaluated natural fine aggregates.

The calorimetric characteristics of the evaluated aggregate sources remained closely aligned with those of the ASTM C778 standard graded-sand control. Cumulative heat at 72 and 168 hours ranged from approximately 99% to 100% of the control, demonstrating that none of the sources produced a material reduction in the overall progression of cement hydration during the measured interval. Greater differentiation occurred in the magnitude and timing of the principal silicate hydration peak. Peak magnitudes ranged from approximately 96% to 107% of the control, while peak times ranged from approximately 100% to 103%. These departures identify modest source-specific differences in early hydration kinetics but do not constitute evidence of sustained suppression of the cement reaction. Cumulative heat at 7 days has been reported as a reliable predictor of strength development [46], [47]; however, the present results indicate that its predictive ability is conditional and the relationship between cumulative heat and strength was generally stronger.

Mine 11057 contained the highest measured organic-carbon content among the evaluated natural fine aggregates at 0.0170%. The principal silicate peak magnitude was approximately 96% of the control, while the corresponding peak time was approximately 103% of the control. Cumulative heat remained approximately 99% of the control at both 72 and 168 hours. The calorimetric record therefore indicates a modest reduction in the maximum rate of silicate hydration and a slight delay in peak development, followed by cumulative reaction progression that remained essentially equivalent to the control.

Table 4-26: Summary of Modified Walkley-Black Organic Carbon, Isothermal Calorimetry Results Normalized to Control, and AASHTO T 71 Strength Ratios for Evaluated Mine Sands

ID	Organic Carbon via MWB (%)	Ratio to Control Cumulative Heat (%) @ 72 hours	Ratio to Control Cumulative Heat (%) @ 168 hours	Ratio to Control Main Calcium Silicate Peak Heat (%)	Ratio to Control Main Calcium Silicate Peak Time (%)	28 day T 71 result U/W (%)
OTT	0%	100%	100%	100%	100%	n/a
16564	0.0011%	99%	99%	96%	102%	99%
16608*	0.0134%	99%	99%	96%	102%	111%
11057**	0.0170%	99%	99%	96%	103%	93%
61377	0.0067%	99%	99%	97%	102%	108%
05455N	0.0145%	100%	100%	98%	103%	115%
05455P	0.0103%	99%	99%	97%	103%	104%

* Fails AASHTO T 21

**Fails AASHTO T 21 and AASHTO T 71

The 28-day AASHTO T 71 unwashed-to-washed strength ratio for mine 11057 was approximately 93%, making it the only evaluated source that failed the prescribed 95% criterion. The calorimetric data alone do not provide a sufficient basis for attributing this failure to severe or persistent inhibition of cement hydration. The comparatively low silicate peak and modest delay in peak development may reflect an interaction between the aggregate and the cementitious system, but the magnitude of those differences was limited and cumulative heat had effectively converged with the control by 72 hours.

The strength deficiency observed for mine 11057 cannot therefore be assigned to organic-carbon content or calorimetric behavior alone. Source-specific physical and chemical characteristics, including gradation, fines distribution, particle packing, surface texture, mineralogy, and soluble constituents, may have contributed individually or collectively to the measured reduction in mortar strength. The available data identify mine 11057 as the source exhibiting the strongest combination of elevated organic carbon, altered early hydration kinetics, and reduced 28-day relative strength, but they do not isolate a single governing mechanism.

The collective findings establish that organic-carbon measurements and calorimetric parameters provide valuable supplemental information for aggregate characterization. Organic carbon quantifies the fraction of oxidizable carbon detected under the prescribed analytical conditions,

while calorimetry resolves changes in the timing and rate of cement hydration. Neither measurement independently predicted the 28-day AASHTO T 71 strength ratio across the evaluated natural fine aggregates. Direct mortar performance testing therefore remains necessary when compliance with the prescribed strength criterion governs aggregate qualification.

A proposed screening sequence based on these findings is as follows. AASHTO T 21 should be retained as the initial screening tool for organic content, as it represents the current standard practice; however, its qualitative nature and chemical selectivity toward humic substances limit its ability to detect all organic compound types, as demonstrated in this study, where sucrose was not captured by the color-based assessment. The modified Walkley-Black method is therefore recommended as a complement, providing a quantitative measurement of organic carbon that is not selective toward a specific organic type and allows for more consistent and objective evaluation. Sands with Organic Carbon below approximately 0.015% are unlikely to produce measurable effects on cement hydration or strength development based on the data evaluated, and no further organic-related testing is recommended for these materials. For sands exceeding this threshold, 3-day isothermal calorimetry should be performed and evaluated against the peak characteristic and cumulative heat thresholds described above. Where calorimetric signatures indicate potential interference, mortar strength testing is recommended as the definitive evaluation, as the variability observed across organic acid types, particularly the cases where cumulative heat recovered while strength did not, indicates that calorimetric data alone cannot confirm mechanical performance to the degree required to accept or reject a mine. This screening sequence balances efficiency with performance sensitivity, reserving the more resource-intensive testing for materials where organic content suggests a meaningful risk of interference.

5. CONCLUSIONS

The concentrations of naturally occurring organic matter in the Florida sands evaluated in this study were generally low therefore the research conclude the following:

- Isothermal conduction calorimetry may serve as a supplemental performance-based characterization method for establishing source-specific hydration-response baselines for sands produced from individual mines. Once a baseline and expected range of variability are established, subsequent calorimetry results may be used to identify changes in cement hydration that warrant additional evaluation, including AASHTO T 71 mortar compressive-strength testing. Isothermal conduction calorimetry should not be used as a stand-alone acceptance criterion, as a statewide threshold applicable across independent aggregate sources, or as a direct quantitative replacement for the AASHTO T 21 color scale, unless additional data establish a defensible performance-based relationship between hydration response and strength performance.
- The modified Walkley–Black method may serve as a supplemental quantitative characterization method for establishing source-specific organic-carbon baselines for sands produced from individual mines. Once a baseline and expected range of variability are established, subsequent MWB results may be used to identify measurable increases in organic carbon that warrant additional evaluation. Such a departure should be interpreted as an indication that additional evaluation is warranted, rather than as direct evidence that the sand is deleterious, and confirmation should rely on a performance-based method such as isothermal conduction calorimetry or AASHTO T 71 mortar strength testing. MWB should not be used as a universal quantitative acceptance criterion, as a statewide threshold applicable across independent aggregate sources, or as a direct quantitative replacement for the AASHTO T 21 color scale.
- Results from isothermal conduction calorimetry testing resulted in behavior consistent with that reported for organic matter at low dosages, as samples with the highest measured organic contents exhibited a slight delay in the main silicate hydration peak.
- A single mechanism linking organic matter in Florida fine aggregates to reductions in concrete performance was not established from this evaluation. Organic matter interacts with cement systems through mechanisms that vary with both compound type and concentration.
- Temporal variability of organic carbon in sands from selected Florida mines was conducted over the evaluation period (2022–2024). The organic content of the evaluated sources was found to be consistent over time within the range of available data.
- Alkaline washing increased sand pH and reduced measured organic content, as confirmed by both AASHTO T 21 and Modified WaLkley Black measurements.
- The ASTM C109 hand-tamped consolidation method produced mortar cubes with lower normalized variability compared to alternative approaches and is recommended for AASHTO T 71 fabrication.

6. RECOMMENDATIONS

Based on the findings of this study, the following recommendations are made:

- AASHTO T 21 should be retained as the primary statewide screening method for identifying potentially deleterious organic impurities in fine aggregate.
- Isothermal conduction calorimetry is recommended as a supplemental performance-based characterization method for establishing source-specific hydration-response baselines for sands produced from individual mines. Subsequent results may be used to identify changes in hydration behavior that warrant additional evaluation, including AASHTO T 71 mortar compressive-strength testing. It should not be used as a stand-alone acceptance criterion or a statewide threshold across independent sources.
- The modified Walkley–Black method is recommended as a supplemental quantitative characterization method for establishing source-specific organic-carbon baselines. Subsequent results may be used to identify measurable increases in organic carbon that warrant additional evaluation. It should not be used as a universal acceptance criterion or a direct replacement for the AASHTO T 21 color scale.
- For fine aggregates with a total organic content in excess of 0.015%, 3-day isothermal calorimetry is recommended as the primary performance-based evaluation tool. Concerns are indicated by a peak magnitude below approximately 90% of control or a peak time delay exceeding approximately 10–15% relative to control. When these thresholds are exceeded, mortar strength testing should be performed. The standard hand-tamped consolidation procedure should be maintained for AASHTO T 71 mortar cube fabrication.

REFERENCES

[1] S. H. Kosmatka and M. Wilson, *Design and Control of Concrete Mixtures*. Portland Cement Association, 2016.

[2] M. C. Garci Juenger and H. M. Jennings, "New insights into the effects of sugar on the hydration and microstructure of cement pastes," *Cement and Concrete Research*, vol. 32, no. 3, pp. 393–399, Mar. 2002, doi: 10.1016/S0008-8846(01)00689-5.

[3] E. Morrison, K. A. Riding, and C. C. Ferraro, "Development of a Test to Quantify Organic Content in Silica Sand," Florida Department of Transportation Research Center, Tallahassee, FL, Technical Memorandum / Final Report Contract No. BEB28, Sep. 2022.

[4] Y. Fang, J. Wang, X. Qian, L. Wang, Y. Dong, and P. Qiao, "Low-cost, ubiquitous biomolecule as a strength enhancer for cement mortars," *Construction and Building Materials*, vol. 311, p. 125305, Dec. 2021, doi: 10.1016/j.conbuildmat.2021.125305.

[5] L. Lang, N. Liu, and B. Chen, "Strength development of solidified dredged sludge containing humic acid with cement, lime and nano-SiO2," *Construction and Building Materials*, vol. 230, p. 116971, Jan. 2020, doi: 10.1016/j.conbuildmat.2019.116971.

[6] J. Zhang, Z. Kang, Y. Yang, B. Dong, and H. Ma, "Enhancement of heat-cured cement paste with tannic acid," *Cement and Concrete Composites*, vol. 137, p. 104931, Mar. 2023, doi: 10.1016/j.cemconcomp.2023.104931.

[7] Z. Luo and B. Zhang, "Effect of humic acid and fulvic acid on mechanical and durability properties of geopolymer stabilized soft soil," *Construction and Building Materials*, vol. 409, p. 133875, Dec. 2023, doi: 10.1016/j.conbuildmat.2023.133875.

[8] *AASHTO T 21. Standard Method of Test for Organic Impurities in Fine Aggregates for Concrete*, Washington, D.C., 2024.

[9] AASHTO T 71, "Standard Method of Test for Effect of Organic Impurities in Fine Aggregate on Strength of Mortar," American Association of State Highway and Transportation Officials, Washington, DC, AASHTO T 71-22, 2022.

[10] "Florida Department of Transportation Standard Specifications for Road and Bridge Construction, FY 2026–27," Tallahassee, Florida, FDOT, 2026.

[11] D. P. Bentz, "Lithium, potassium and sodium additions to cement pastes," *Advances in Cement Research*, vol. 18, no. 2, pp. 65–70, Apr. 2006, doi: 10.1680/adcr.2006.18.2.65.

[12] L. Huang and P. Yan, "Effect of alkali content in cement on its hydration kinetics and mechanical properties," *Construction and Building Materials*, vol. 228, p. 116833, Dec. 2019, doi: 10.1016/j.conbuildmat.2019.116833.

[13] I. Jawed and J. Skalny, "Alkalies in cement: A review," *Cement and Concrete Research*, vol. 8, no. 1, pp. 37–51, Jan. 1978, doi: 10.1016/0008-8846(78)90056-X.

[14] E. A. Ghabbour *et al.*, "Isolation of humic acid from the brown alga Pilayella littoralis," *Journal of applied phycology*, vol. 6, no. 5, pp. 459–468, 1994.

[15] M. H. Hayes and R. Swift, "The chemistry of soil organic colloids," *The chemistry of soil constituents*, pp. 179–320, 1978.

[16] E. Allahkarami, E. Allahkarami, B. Rezai, and A. Azadmehr, "Advancing humic acids extraction procedures: A review of methods, innovations, and sustainability challenges," *Separation and Purification Technology*, vol. 376, p. 133954, Dec. 2025, doi: 10.1016/j.seppur.2025.133954.

[17] A. G. Zavarzina, N. N. Danchenko, V. V. Demin, Z. S. Artemyeva, and B. M. Kogut, "Humic Substances: Hypotheses and Reality (a Review)," *Eurasian Soil Sc.*, vol. 54, no. 12, pp. 1826–1854, Dec. 2021, doi: 10.1134/S1064229321120164.
[18] M. H. B. Hayes, R. Mylotte, and R. S. Swift, "Humin," in *Advances in Agronomy*, vol. 143, Elsevier, 2017, pp. 47–138. doi: 10.1016/bs.agron.2017.01.001.
[19] M. Keppert, M. Jerman, L. Scheinherrová, P. Reiterman, B. Doušová, and R. Černý, "Influence of free and sorbed zinc on cement hydration," *J Therm Anal Calorim*, vol. 138, no. 3, pp. 1935–1943, Nov. 2019, doi: 10.1007/s10973-019-08200-0.
[20] US EPA, *Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry*, Data and Tools, Cincinnati, OH., 1994.
[21] Florida Department of Transportation, "Florida Method of Test for pH of Soil and Water," Florida Department of Transportation, Gainesville, Florida, FM 5-550, Mar. 2023.
[22] "Thin Cement-Based Composites for Efficient Neutron Attenuation," *MJ*, vol. 122, no. 4, Jul. 2025, doi: 10.14359/51746803.
[23] *ASTM C1702. Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry*, West Conshohocken, PA., 2017.
[24] D. J. Greenland and M. H. B. Hayes, Eds., *The chemistry of soil constituents*. in A Wiley-Interscience publication. Chichester: Wiley, 1978.
[25] W. Zhu, C. F. Chiu, C.-L. Zhang, and K.-L. Zeng, "Effect of humic acid on the behaviour of solidified dredged material," *Can. Geotech. J.*, vol. 46, no. 9, pp. 1093–1099, Sep. 2009, doi: 10.1139/T09-045.
[26] M. M. Kononova, *Soil Organic Matter*. Pergamon, 1966.
[27] H. Tremblay, J. Duchesne, J. Locat, and S. Leroueil, "Influence of the nature of organic compounds on fine soil stabilization with cement," *Can. Geotech. J.*, vol. 39, no. 3, pp. 535–546, Jun. 2002, doi: 10.1139/t02-002.
[28] D. R. Klein, *Organic chemistry*, Fourth edition. Hoboken, NJ: Wiley, 2021.
[29] J. H. Taplin, "Discussion of H. E. Vivian, 'Some chemical additions and admixtures in cement paste and concrete,'" in *Proceedings of the Fourth International Symposium on the Chemistry of Cement, Washington, 1960*, in National Bureau of Standards Monograph. Washington, DC: U.S. Department of Commerce, 1962, pp. 924–925.
[30] J. D. Birchall and N. L. Thomas, "The mechanism of retardation of setting of OPC by sugars," in *British Ceramic Proceedings*, British Ceramic Society, 1984, pp. 305–315.
[31] N. L. Thomas and J. D. Birchall, "The retarding action of sugars on cement hydration," *Cement and Concrete Research*, vol. 13, no. 6, pp. 830–842, Nov. 1983, doi: 10.1016/0008-8846(83)90084-4.
[32] N. L. Thomas and J. D. Birchall, "A Reply to a Discussion by S. Chatterji of `The retarding action of sugars on cement hydration'," *Cement and Concrete Research*, vol. 14, no. 5, pp. 761–762, 1984, doi: 10.1016/0008-8846(84)90035-7.
[33] P. D. Tennis and H. M. Jennings, "A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes," *Cement and Concrete Research*, vol. 30, no. 6, pp. 855–863, Jun. 2000, doi: 10.1016/S0008-8846(00)00257-X.

[34] G. Constantinides and F.-J. Ulm, “The effect of two types of C-S-H on the elasticity of cement-based materials: Results from nanoindentation and micromechanical modeling,” *Cement and Concrete Research*, vol. 34, no. 1, pp. 67–80, Jan. 2004, doi: 10.1016/S0008-8846(03)00230-8.
[35] R. Kumar and B. Bhattacharjee, “Porosity, pore size distribution and in situ strength of concrete,” *Cement and Concrete Research*, vol. 33, no. 1, pp. 155–164, Jan. 2003, doi: 10.1016/S0008-8846(02)00942-0.
[36] D. A. Abrams, “Effect of Tannic Acid on the Strength of Concrete,” Structural Materials Research Laboratory, Lewis Institute, Chicago, IL, Bulletin 7, 1920.
[37] B. H. Cruz, J. M. Díaz-Cruz, C. Ariño, and M. Esteban, “Heavy Metal Binding by Tannic Acid: A Voltammetric Study,” *Electroanalysis*, vol. 12, no. 14, pp. 1130–1137, Oct. 2000, doi: 10.1002/1521-4109(200010)12:14<1130::AID-ELAN1130>3.0.CO;2-7.
[38] J. Buschmann and L. Sigg, “Antimony(III) Binding to Humic Substances: Influence of pH and Type of Humic Acid,” *Environ. Sci. Technol.*, vol. 38, no. 17, pp. 4535–4541, Sep. 2004, doi: 10.1021/es049901o.
[39] E. Tipping, *Cation Binding by Humic Substances*, 1st ed. Cambridge University Press, 2002. doi: 10.1017/CBO9780511535598.
[40] S. Saride, A. J. Puppala, and S. R. Chikyala, “Swell-shrink and strength behaviors of lime and cement stabilized expansive organic clays,” *Applied Clay Science*, vol. 85, pp. 39–45, Nov. 2013, doi: 10.1016/j.clay.2013.09.008.
[41] H. Chen and Q. Wang, “The behaviour of organic matter in the process of soft soil stabilization using cement,” *Bull Eng Geol Environ*, vol. 65, no. 4, pp. 445–448, Nov. 2006, doi: 10.1007/s10064-005-0030-1.
[42] AASHTO T 27, *Standard Method of Test for Sieve Analysis of Fine and Coarse Aggregates*, AASHTO T 27, 2014.
[43] M. Wang *et al.*, “Effect of humic substances on the fraction of heavy metal and microbial response,” *Sci Rep*, vol. 14, no. 1, p. 11206, May 2024, doi: 10.1038/s41598-024-61575-5.
[44] Z. Guo *et al.*, “Humic Acid Enhances Soil Fertility and Microbial Diversity Under Optimized Nitrogen Fertilization in Quinoa Rhizosphere,” *Plants (Basel)*, vol. 14, no. 24, p. 3850, Dec. 2025, doi: 10.3390/plants14243850.
[45] Muñoz Jose F., Balachandran, Chandni, Shastry, Anant, and Meininger, Richard C., “FTIR and TG Analysis of Organic Impurities in Fine Aggregates from Florida DOT,” Federal Highway Administration, Feb. 2020.
[46] D. P. Bentz, T. Barrett, I. De La Varga, and W. J. Weiss, “Relating Compressive Strength to Heat Release in Mortars,” *Adv. Civ. Eng. Matls.*, vol. 1, no. 1, p. 20120002, Sep. 2012, doi: 10.1520/ACEM20120002.
[47] Z. Li, D. Lu, and X. Gao, “Analysis of correlation between hydration heat release and compressive strength for blended cement pastes,” *Construction and Building Materials*, vol. 260, p. 120436, Nov. 2020, doi: 10.1016/j.conbuildmat.2020.120436.

APPENDIX A - Draft Florida Standard Test Method for Qualification of Fine Aggregates Containing Organic Impurities Using Isothermal Conduction Calorimetry

Designation: FM XXXX

A. *Basis: Adapted from the measurement concept of ASTM C1702/C1702M for isothermal conduction calorimetry, modified for mortar systems used to evaluate fine aggregate organic effects.*

1. Scope

1.1 This method covers a laboratory procedure for qualifying fine aggregate sources, or fine aggregate production lots, with respect to the influence of organic impurities on early cement hydration using isothermal conduction calorimetry.

1.2 The method measures heat-flow rate and cumulative heat from cement mortar mixtures containing the subject sand and compares those results with a control mortar prepared with ASTM C778 standard graded.

1.3 The method is intended as a performance-based complement to visual/colorimetric screening for organic impurities and to mortar strength testing. It is not intended to identify the chemical species responsible for retardation or suppression of hydration.

1.4 The default test duration is 72 h (3 days).

1.5 The values stated in SI units are to be regarded as standard. Inch-pound units may be shown for information only.

1.6 This method does not purport to address all safety concerns. It is the responsibility of the user to establish appropriate safety, health, and environmental practices before use.

2. Apparatus

2.1 Isothermal Conduction Calorimeter. The calorimeter shall maintain the selected test temperature within ±1 °C and record thermal power at intervals not greater than 30 s. It shall have a minimum sensitivity of 100 μJ/s and sufficient stability, with low baseline drift and noise, to ensure reliable measurement of thermal power.

2.1.1 Reference Channel. The calorimeter reference channel shall be loaded with a reference specimen (Section 3.5) seated in an ampoule. The mass of the reference specimen shall be selected such that the heat capacity of the reference ampoule and specimen assembly matches that of the test ampoule and mortar mixture assembly, and such that the mortar mixture contains no less than 3 g of cementitious material.

2.2 Devices for measuring, transferring, and loading the individual constituents (e.g., cement, water, SCMs, and admixtures) into the specimen vial or ampoule.

2.3 Sample ampoules or sample cups, sealable and compatible with the calorimeter. All samples in a comparison set shall use the same cup type, lid type, sample mass, and loading procedure.

2.4 Balance, readable to 0.01 g for cement, water, and sand masses used in calorimeter specimens.

2.5 Vortex type mixing device.

2.6 Data acquisition and analysis software capable of recording thermal power, integrating cumulative heat, and exporting data in tabular form.

3. Materials

3.1 Subject sand. the fine aggregate source or production lot being evaluated.

3.2 Cement. Use a single lot of portland cement meeting ASTM C150/C150M unless another cementitious system is specified by the agency. The same cement shall be used for all specimens in a comparison set.

3.3 Water. Use potable water or reagent water. The same water shall be used for all specimens in a comparison set.

3.4 Control sand. Use ASTM C778 standard graded sand as the control aggregate.

3.5 Reference specimen. An inert material with a known heat capacity.

NOTE 1 — When the purpose is to evaluate soluble organics, the agency may require a leachate-contact procedure in which mixing water is preconditioned with the subject sand. That option should be validated separately before acceptance decisions are made.

4. Sample Preparation

4.1 Sand:

4.1.1 Obtain a representative sand sample and reduce it to test size without preferentially removing lightweight organic particles.

4.1.2 Remove particles larger than the agency-defined maximum size for the calorimeter mortar. Unless otherwise specified, use the portion passing the 4.75 mm sieve.

4.1.3 Determine the moisture absorption of the subject sand according to FM 1-T084.

4.1.4 On the day of mixing, determine the surface dry moisture content of the subject sand in accordance with AASHTO T 255.

4.1.5 Do not oven-dry the as-received subject sand unless oven drying is part of the agency qualification condition. Heating may alter organic compounds and change the measured effect.

4.2 Bring cement, water, sand, mixing tools, sample cups, and calorimeter channels to the test temperature before mixing unless the calorimeter manufacturer provides an equivalent conditioning procedure.

5. Procedure

5.1 Calorimeter verification. Verify calorimeter operation using the manufacturer calibration procedure and a reference material or reference cement acceptable to the laboratory quality system. Do not begin qualification testing until baseline stability and channel agreement are within laboratory control limits.

5.2 Test matrix. For each sand qualification, prepare at least duplicate specimens for: (a) control mortar with ASTM C778 sand, and (b) subject mortar with as-received sand.

5.3 Batch Quantity Determination. Proportion the mortar using a default mass ratio of 1:1:0.5 (cement:sand:water). To determine actual batch masses, compute the scalar that equates the thermal mass of the mortar and ampoule assembly to that of the reference ampoule and specimen assembly. Multiply each default proportion by this scalar to obtain final batch masses. Specific heat capacity values for each constituent and ampoule material are given in Table A-1. The total wet sample mass shall be the same for all specimens within ±0.1 g and shall fall within the calorimeter manufacturer recommended range. Do not include chemical admixtures unless specifically required by the agency; if used, dosage shall be held constant by mass of cement and reported.

NOTE 2 — If the sand grading or particle size makes the default proportion unsuitable for the calorimeter ampoule, a reduced sand-cement ratio may be used. The selected proportion shall be documented and applied consistently to the control and subject sand mortars.

Table A-1: Specific Heat Capacities Cementitious Contents

Material	Specific Heat Capacity, J/g*k
Cement, portland unhydrated	0.75
Fly Ash	0.8
Sand	0.8
Water	4.18

5.4 Weighing. Weigh sand and cement directly into the ampoule to the nearest 0.001 g. Weigh mix water separately into a suitable container. Each constituent shall be within ±0.002 g of the target batch mass.

5.5 Mixing and Loading. Begin data logging prior to mixing. Add the mix water to the ampoule containing the dry constituents. Start timing at initial water-cement contact. Mix using a vortex mixer at 2500 RPM for 5 seconds. Seal the ampoule immediately after mixing and place it into the calorimeter channel adjacent to the reference ampoule. The elapsed time from water-cement contact to calorimeter loading shall not exceed 2 minutes and shall be recorded for all specimens.

5.6 Measurement. Maintain the test temperature at 23.0 ± 1°C unless another temperature is specified. Run the test for a minimum of 72 hours.

NOTE 3 — Tests may be extended to 168 hours where additional hydration data are required.

5.7 Replication. Conduct each comparison set concurrently when possible. When the number of calorimeter channels is limited, rotate control and subject specimens among channels and use a laboratory control chart to account for channel effects.

5.8 Data screening. Exclude data only for documented procedural errors, cup leakage, gross mass error, instrument malfunction, or obvious disturbance. Do not exclude a specimen solely because it shows retardation or low heat release.

5.9 Duplicate Acceptance. Evaluate duplicate agreement prior to calculating results. Acceptance criteria for duplicate specimens are given in Section 9.

6. Calculations

6.1 Normalize thermal power to the mass of cement in the calorimeter specimen and report in mW/g cement, unless the agency requires normalization to total binder mass.

6.2 Determine cumulative heat by numerical integration of the normalized thermal power curve and report in J/g cement at 12 h, 24 h, 48 h and 72 h

6.3 Determine the time and magnitude of the main hydration peak. When more than one peak occurs, report all peaks and identify the peak used for the qualification decision.

6.4 For each condition, average the results of accepted duplicate specimens before computing the following ratios.

6.5 Calculate the cumulative heat ratio at age t as a percentage of the control: $CHR_t = \frac{H_{subject}}{H_{control}} \times 100$

Where:

- $H_{subject}$= cumulative heat of the subject mortar at age t, in J/g cement
- $H_{control}$= cumulative heat of the control mortar at age t, in J/g cement

6.6 Calculate the peak heat-flow ratio as a percentage of the control: $PHR = \frac{P_{subject}}{P_{control}} \times 100$

Where:

- $P_{control}$= peak heat-flow rate of the control mortar, in mW/g cement

6.7 Calculate the retardation time as: $RT = t_{subject} - t_{control}$

7. Qualification

7.1 This method is intended to be used in conjunction with AASHTO T 21 and the modified Walkley-Black organic carbon test as part of a screening sequence. A positive or borderline result from AASHTO T 21 or a organic carbon content exceeding approximately 0.015% indicates the presence of organic matter that may be detrimental to the cement system. Calorimetric evaluation then determines whether the organic matter present is hydration-active at a concentration sufficient to warrant concern. Where calorimetric thresholds are exceeded, there is a likelihood of adverse effects on strength and field performance, and mortar strength testing in accordance with AASHTO T 71 is recommended as the definitive evaluation.

7.1 A sand qualifies when the duplicate average satisfies the criteria in Table A-2 and no individual specimen indicates an obvious deleterious hydration response. The agency may modify the numerical thresholds after validating this method against AASHTO T 71 strength performance, concrete setting time, field performance, or other acceptance data.

7.2 If the subject sand fails the AASHTO T 71 comparison the sand shall not be qualified for use without mitigation, blending, washing, source control, or additional performance testing acceptable to the agency.

7.4 If duplicate variability exceeds the limits in Table 2, repeat the test unless the agency determines that the variability itself is evidence of nonuniform material.

Table A-2: Proposed Default Qualification Criteria for Organic effects

Index	Default Criterion	Primary Interpretation	Action if Not Met
Cumulative heat ratio at 72 h, CHR72	>= 95%	Hydration extent at 3 days is not materially reduced.	Perform AASHTO T 71 mortar strength testing.

Index	Default Criterion	Primary Interpretation	Action if Not Met
Peak heat-flow ratio, PHR	>= 90%	Main hydration reaction rate is not significantly suppressed.	Perform AASHTO T 71 mortar strength testing.
Retardation time, RT	<= 2.0 h or <= 15% of control peak time, whichever is greater	Set-related delay is limited.	Consider setting time verification; perform mortar strength testing.
Duplicate CV for CHR72	<= 10%	Specimen preparation and sand uniformity are acceptable.	Repeat test or resample material.

NOTE 4 — Where extended hydration monitoring is required, tests may be run for up to 168 hours. Cumulative heat recovery at 72 h alone is not sufficient to confirm acceptable mechanical performance; for certain organic types, cumulative heat may recover while compressive strength does not.

8. Report

- Sand identification, source, production lot, sampling date, and sample reduction procedure.
- Whether the subject sand was tested as received, washed, dried, preconditioned, or otherwise altered before testing.
- Cement type, cement source, lot number, mill certificate information if available, and water source.
- Mixture proportions, sample mass, moisture corrections, mixing procedure, elapsed time from water-cement contact to calorimeter loading, cup type, and test temperature.
- Number of replicate specimens and calorimeter channel identification for each specimen.
- Thermal power curves and cumulative heat curves for the control, subject sand, and washed companion where applicable.
- Cumulative heat at 12 h, 24 h, 48 h, 72 h, and 168 h; main peak time; peak heat-flow rate; heat ratios; peak ratios; retardation index; duplicate statistics.
- Qualification determination: qualified, conditionally qualified pending additional testing, or not qualified.
- Any deviations from this method and any observed anomalies such as cup leakage, segregation, abnormal noise, or high duplicate variability.

9. Precision and Bias

9.1 A precision and bias statement has not yet been established for this draft method.

9.2 Expected precision depends on calorimeter stability, channel calibration, sample mass, elapsed loading time, uniformity of sand moisture correction, repeatability of mixing, and consistency of the cement used for comparison testing.

9.3 Until a multi-laboratory precision statement is developed, each laboratory shall maintain control charts for the ASTM C778 control mortar, including cumulative heat at 24 h, 72 h, and 168 h and the time of the main hydration peak.

9.4 Bias cannot be determined because there is no accepted reference value for the effect of organic impurities in a given fine aggregate on cement hydration.

ANNEX A1 - EXAMPLE DATA REDUCTION

A1.1 Export thermal power data as time and normalized thermal power. Correct the time axis so that time zero corresponds to initial water-cement contact.

A1.2 Integrate the thermal power curve using the trapezoidal rule to obtain cumulative heat at the specified ages.

A1.3 Identify the main hydration peak using the maximum heat-flow rate after the dormant period. Where noisy data prevent clear identification, smooth the data using a documented method that does not shift the peak time by more than 0.1 h.

A1.4 Prepare a comparison plot showing control, subject sand, and washed companion curves on the same axes. Qualification should be based on both tabulated indices and visual review of the curves.

APPENDIX X1 - COMMENTARY

X1.1 ASTM C1702/C1702M and ASTM C1679/C1679M provides the foundation for controlled isothermal heat measurement of hydraulic cementitious materials. This Florida Method draft preserves the core calorimetry concept but changes the material system from cement paste heat-of-hydration measurement to comparative mortar screening for fine aggregate organic effects.

X1.2 AASHTO T 21 is a qualitative colorimetric warning test selective toward humic substances; it does not detect all organic compounds relevant to cement hydration. The modified Walkley-Black method complements AASHTO T 21 by providing a quantitative measure of organic carbon not selective toward a specific organic type. Where AASHTO T 21 or modified Walkley-Black results indicate the presence of organic matter, the calorimetric approach in this method provides an earlier, hydration-based indicator of whether those organics are active enough to warrant concern, and can be correlated to AASHTO T 71 strength performance or agency performance requirements.

APPENDIX B - Raw Data and Statistical Analysis

Table B-1: Raw Data of Strength for Each Mine

FDOT MINE ID	Age (Days)	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)
05455N	3	3076	16608	3	2977	61377	3	3417
05455N	3	3138	16608	3	2909	61377	3	3417
05455N	3	3254	16608	3	2774	61377	3	3617
05455N	7	3901	16608	7	4283	61377	7	4192
05455N	7	3619	16608	7	3874	61377	7	4447
05455N	7	4116	16608	7	4097	61377	7	4673
05455N	28	5774	16608	28	6084	61377	28	5747
05455N	28	6388	16608	28	6042	61377	28	6083
05455N	28	6630	16608	28	6032	61377	28	5938
05455N-W	3	3006	16608W	3	3474	61377W	3	3089
05455N-W	3	2985	16608W	3	3553	61377W	3	3124
05455N-W	3	3237	16608W	3	3383	61377W	3	3175
05455N-W	7	3733	16608W	7	4013	61377W	7	4039
05455N-W	7	3997	16608W	7	4316	61377W	7	4212
05455N-W	7	3784	16608W	7	4200	61377W	7	3954
05455N-W	28	5627	16608W	28		61377W	28	5403
05455N-W	28	5439	16608W	28		61377W	28	5724
05455N-W	28	5305	16608W	28		61377W	28	5250
16564	3	2443	11057	3	2957	05455P	3	3075
16564	3	3140	11057	3	2715	05455P	3	3081
16564	3	3067	11057	3	2892	05455P	3	3237
16564	7	4133	11057	7	3895	05455P	7	3973
16564	7	4122	11057	7	3680	05455P	7	3838
16564	7	4069	11057	7	3564	05455P	7	3919
16564	28	5629	11057	28	4385	05455P	28	5276
16564	28	6190	11057	28	4452	05455P	28	5518
16564	28	6134	11057	28	4464	05455P	28	5554
16564W	3	3541	11057W	3	2704	05455P-W	3	3205
16564W	3	3514	11057W	3	2525	05455P-W	3	3300
16564W	3	3448	11057W	3	2544	05455P-W	3	3122
16564W	7	4212	11057W	7	3072	05455P-W	7	4373
16564W	7	4215	11057W	7	3270	05455P-W	7	4088
16564W	7	4221	11057W	7	3188	05455P-W	7	4191
16564W	28	6194	11057W	28	4942	05455P-W	28	5501
16564W	28	5932	11057W	28	4967	05455P-W	28	5396

FDOT MINE ID	Age (Days)	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)
16564W	28	6006	11057W	28	5197	05455P-W	28	4864

Table B-2: Raw Cube Data of Dosed Sand

FDOT MINE ID	Age (Days)	Organic Replacement %	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)
T-.01-1	3	0.01%	2817	F.01-1	3	1864	H.01-1	3	1781
T.01-2	3	0.01%	2835	F.01-2	3	1527	H.01-2	3	2043
T.01-3	3	0.01%	2807	F.01-3	3	1208	H.01-3	3	1735
T.01-4	7	0.01%	3598	F.01-4	7	3869	H.01-4	7	3271
T.01-5	7	0.01%	3475	F.01-5	7	3001	H.01-5	7	2269
T.01-6	7	0.01%	3749	F.01-6	7	3414	H.01-6	7	2631
T.01-7	28	0.01%	3627	F.01-7	28	4144	H.01-7	28	4215
T.01-8	28	0.01%	3912	F.01-8	28	4010	H.01-8	28	4090
T.01-9	28	0.01%	3828	F.01-9	28	4193	H.01-9	28	4311
T.06-1	3	0.06%	2475	F.06-1	3	1496	H.06-1	3	2187
T.06-2	3	0.06%	2237	F.06-2	3	1501	H.06-2	3	2427
T.06-3	3	0.06%	2305	F.06-3	3	1376	H.06-3	3	2179
T.06-4	7	0.06%	3754	F.06-4	7	1645	H.06-4	7	2380
T.06-5	7	0.06%	3666	F.06-5	7	1955	H.06-5	7	2790
T.06-6	7	0.06%	3420	F.06-6	7	2214	H.06-6	7	2745
T.06-7	28	0.06%	4692	F.06-7	28	3230	H.06-7	28	4338
T.06-8	28	0.06%	3661	F.06-8	28	3071	H.06-8	28	4194
T.06-9	28	0.06%	3939	F.06-9	28	3509	H.06-9	28	4227
T.15-1	3	0.15%	307	F.15-1	3	0	H.15-1	3	1854
T.15-2	3	0.15%	296	F.15-2	3	0	H.15-2	3	2289
T.15-3	3	0.15%	325	F.15-3	3	0	H.15-3	3	2183
T.15-4	7	0.15%	3087	F.15-4	7	1976	H.15-4	7	2872
T.15-5	7	0.15%	3110	F.15-5	7	1898	H.15-5	7	2701
T.15-6	7	0.15%	3056	F.15-6	7	1991	H.15-6	7	2843
T.15-7	28	0.15%	4346	F.15-7	28	2353	H.15-7	28	4075
T.15-8	28	0.15%	4326	F.15-8	28	2667	H.15-8	28	3747
T.15-9	28	0.15%	3489	F.15-9	28	2862	H.15-9	28	4020
T.30-1	3	0.30%	0	F.30-1	3	0	H.30-1	3	1538
T.30-2	3	0.30%	0	F.30-2	3	0	H.30-2	3	1495
T.30-3	3	0.30%	0	F.30-3	3	0	H.30-3	3	1457
T.30-4	7	0.30%	0	F.30-4	7	639	H.30-4	7	2371
T.30-5	7	0.30%	0	F.30-5	7	671	H.30-5	7	2364

FDOT MINE ID	Age (Days)	Organic Replacement %	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)	FDOT MINE ID	Age (Days)	Strength (psi)
T.30-6	7	0.30%	0	F.30-6	7	665	H.30-6	7	2274
T.30-7	28	0.30%	0	F.30-7	28	950	H.30-7	28	3208
T.30-8	28	0.30%	0	F.30-8	28	1017	H.30-8	28	3073
T.30-9	28	0.30%	0	F.30-9	28	1251	H.30-9	28	3158

Table B-3: Data and ANOVA Results From Figure 4-4 - Organic Carbon vs. Color Rating

Mine ID	% of Organic Carbon	T 21 Score
16564U	0.0011%	1
16608U	0.0134%	5
11057U	0.0170%	5
61377U	0.0067%	1
05455N	0.0145%	2
05455P	0.0103%	1
16564W	0.0029%	1
16608W	0.0014%	1
11057W	0.0059%	1
61377W	0.0045%	1
05455N-W	0.0136%	1
05455P-W	0.0097%	1
Multiple R	0.652989309	
R Square	0.426395037	
P- Value	0.021322465	

Table B-4: Data and ANOVA Results from Figure 4-5 - Organic Carbon (MWB) vs. Total Carbon by (EA)

Mine ID	Sieve Size	Organic Carbon % (MWB)	Total Carbon % (EA)
16564U	#16	0.0003	0
16608U	#16	0.0050	0.03
11057U	#16	0.0054	0.01
61377U	#16	0.0013	0
05455N	#16	0.0166	0.01
05455P	#16	0.0103	0
16564U	#30	0.0003	0
16608U	#30	0.0056	0.01
11057U	#30	0.0066	0.01
61377U	#30	0.0020	0
05455N	#30	0.0056	0.02
05455P	#30	0.0055	0
16564U	#50	0.0006	0
16608U	#50	0.0112	0.01
11057U	#50	0.0133	0.02
61377U	#50	0.0034	0.01
05455N	#50	0.0077	0.02
05455P	#50	0.0072	0.01
16564U	#100	0.0013	0
16608U	#100	0.0154	0.04
11057U	#100	0.0222	0.04
61377U	#100	0.0033	0.01
05455N	#100	0.0105	0.02
05455P	#100	0.0096	0.02
16564U	Bulk	0.0013	0
16608U	Bulk	0.0124	0.03
11057U	Bulk	0.0130	0.04
61377U	Bulk	0.0044	0.01
05455N	Bulk	0.0120	0.04
05455P	Bulk	0.0077	0.02
Multiple R	0.736594		
R Square	0.54257		
P- Value	3.47E-06		

Table B-5: Data and ANOVA Results From Figure 4-6 - pH vs. Organic Carbon

Mine ID	pH	% of Organic Carbon
16564U	8.93	0.0011%
16608U	7.63	0.0134%
11057U	7.93	0.0170%
61377U	8.28	0.0067%
05455N	8.12	0.0145%
05455P	8.85	0.0103%
16564W	9.48	0.0029%
16608W	8.63	0.0014%
11057W	9.38	0.0059%
61377W	9.2	0.0045%
05455N-W	8.85	0.0136%
05455P-W	8.68	0.0097%
Multiple R	0.663093	
R Square	0.439693	
P- Value	0.018752	

Table B-6: Data and ANOVA Results From Figure 4-7 pH vs. T 21

Mine ID	pH	T 21 Score
16564U	8.93	1
16608U	7.63	5
11057U	7.93	5
61377U	8.28	1
05455N	8.12	2
05455P	8.85	1
16564W	9.48	1
16608W	8.63	1
11057W	9.38	1
61377W	9.2	1
05455N-W	8.85	1
05455P-W	8.68	1
Multiple R	0.776552	
R Square	0.603033	
P- Value	0.002973	

Table B-7: Data and ANOVA Results From Figure 4-8 - Color vs. 7 Day T71

Mine ID	Color	7-day T 71
16564	1	98%
16608	5	98%
11057	5	112%
61377	1	109%
05455N	2	101%
05455P	1	93%
Multiple R	0.342222	
R Square	0.117116	
P- Value	0.506706	

Table B-8: Data and ANOVA Results From Figure 4-9 - Color vs. 28 Day T71

Mine ID	Color	28-day T 71
16564	1	98%
16608	5	98%
11057	5	112%
61377	1	109%
05455N	2	101%
05455P	1	93%
Multiple R	0.342222	
R Square	0.117116	
P- Value	0.506706	

Table B-9: Data and ANOVA Results From Figure 4-10 - MWB vs. 7 Day T71

Mine ID	Organic Carbon %	7-day T 71
16564	0.0011%	99%
16608	0.0134%	111%
11057	0.0170%	93%
61377	0.0067%	108%
05455N	0.0145%	115%
05455P	0.0103%	104%
Multiple R	0.294689941	
R Square	0.086842161	
P- Value	0.570760844	

Table B-10: Data and ANOVA Results From Figure 4-11 – MWB vs. 28 Day T71

Mine ID	Organic Carbon %	28-day T 71
16564	0.0011%	99%
16608	0.0134%	111%
11057	0.0170%	93%
61377	0.0067%	108%
05455N	0.0145%	115%
05455P	0.0103%	104%
Multiple R	0.088049929	
R Square	0.00775279	
P- Value	0.868266423	

Table B-11: Data and ANOVA Results From Figure 4-12 - pH vs. 7 Day T71

Mine ID	pH	7-day T 71
16564	8.93	98%
16608	7.63	98%
11057	7.93	112%
61377	8.28	109%
05455N	8.12	101%
05455P	8.85	93%
Multiple R	0.452993	
R Square	0.205203	
P- Value	0.043622	

Table B-12: Data and ANOVA Results From Figure 4-13 - pH vs. 28 Day T71

Mine ID	pH	28-day T 71
16564	8.93	99%
16608	7.63	111%
11057	7.93	93%
61377	8.28	108%
05455N	8.12	115%
05455P	8.85	104%
Multiple R	0.273699	
R Square	0.074911	
P- Value	0.599703	

Table B-13: Data and ANOVA Results From Figure 4-14 - MWB vs. 28 Day Strength

Mine ID	% of Organic Carbon	28-day Strength (psi)
16564U	0.00%	5980
16608U	0.01%	6050
11057U	0.02%	4700
61377U	0.01%	5920
05455N	0.01%	6260
05455P	0.01%	5450
16564W	0.00%	6040
16608W	0.00%	5470
11057W	0.01%	5040
61377W	0.00%	5460
05455N-W	0.01%	5460
05455P-W	0.01%	5254
Multiple R	0.207822952	
R Square	0.043190379	
P- Value	0.516891543	

Table B-14: Data and ANOVA Results From Figure 4-15- pH vs. 28 Day Strength

Mine ID	pH	28-day Strength (psi)
16564U	8.93	5980
16608U	7.63	6050
11057U	7.93	4700
61377U	8.28	5920
05455N	8.12	6260
05455P	8.85	5450
16564W	9.48	6040
16608W	8.63	5470
11057W	9.38	5040
61377W	9.2	5460
05455N-W	8.85	5460
05455P-W	8.68	5254
Multiple R	0.120710944	
R Square	0.014571132	
P- Value	0.708634124	

Table B-15: Raw Data For Mine Sands Calorimetry and ANOVA Results From Figure 4-16 to Figure 4-23

Mine ID	Main Calcium Silicate Peak Heat (mW/g)	Main Calcium Silicate Peak Time (h)	Secondary Aluminate Peak Heat (mW/g)	Secondary Aluminate Peak Time (h)	Cumulative Heat (J/g) @ 72 hours	Cumulative Heat (J/g) @ 168 hours	Cumulative Heat (J/g) @ 405 hours
OTT-1	3.71	8.35	3.49	10.86	262.22	309.94	343.11
OTT-2	3.69	8.35	3.45	10.86	258.62	306.31	339.26
16564-1	3.57	8.55	3.37	11.06	256.61	303.58	334.13
16564-2	3.57	8.55	3.38	11.06	257.01	303.9	334.19
16608-1	3.54	8.55	3.35	10.89	256.2	303.48	334.08
16608-2	3.55	8.55	3.37	10.89	257.77	305.19	336.12
11057-1	3.57	8.71	3.4	11.06	257.59	305.02	335.71
11057-2	3.57	8.55	3.4	10.89	257.89	305.51	336.33
61377-1	3.58	8.55	3.41	10.89	257.86	305.33	336.43
61377-2	3.58	8.55	3.4	10.89	256.65	304.25	334.92
05455N-1	3.63	8.61	3.4	11.01	260.22	307.13	337.39
05455N-2	3.63	8.61	3.4	11.01	259.85	306.94	337.27
05455P-1	3.59	8.61	3.35	11.17	258.63	305.34	335.37
05455P-2	3.59	8.61	3.38	11.17	259.04	306.14	336.76
3-day Heat and Strength	Multiple R	0.245812408			3-day Heat and Organic Carbon (%)	Multiple R	0.2837218
	R Square	0.06042374				R Square	0.08049806
	P- Value	0.63870784				P- Value	0.495881006
7-day Heat and Strength	Multiple R	0.414907457			7-day Heat and Organic Carbon (%)	Multiple R	0.39680943
	R Square	0.172148198				R Square	0.157457724
	P- Value	0.413351599				P- Value	0.33039393
19-day Heat and 28 day-Strength	Multiple R	0.049409118			19-day Heat and Organic Carbon (%)	Multiple R	0.691940798
	R Square	0.002441261				R Square	0.478782068
	P- Value	0.925946634				P- Value	0.127733226
Main Silicate Peak and Organic Carbon (%)	Multiple R	0.608157953			Main Silicate Peak Time and Organic Carbon (%)	Multiple R	0.672394618
	R Square	0.369856096				R Square	0.452114523
	P- Value	0.109670468				P- Value	0.067718356

Table B-16: Raw Data from Isothermal Calorimetry on Dosed Sands

Mine ID	Main Calcium Silicate Peak Heat (mW/g)	Main Calcium Silicate Peak Time (h)	Cumulative Heat (J/g) @ 72 hours	Cumulative Heat (J/g) @ 168 hours
C-0 (1)	2.37	6.67	179.58	209.70
C-0 (2)	2.38	6.73	179.55	210.04
H-0.01 (1)	2.28	7.19	178.25	208.76
H-0.01 (2)	2.30	6.76	179.98	210.37
H-0.06 (1)	2.33	7.75	184.47	215.92
H-0.06 (2)	2.36	7.85	187.04	218.65
H-0.15 (1)	2.68	9.88	220.28	261.44
H-0.15 (2)	2.21	11.18	179.40	212.11
H-0.30 (1)	2.07	20.24	171.75	208.00
H-0.30 (2)	2.06	20.38	172.76	209.37
T-0.01 (1)	2.15	13.74	179.18	213.86
T-0.01 (2)	2.12	16.35	172.66	207.67
T-0.06 (1)	1.89	69.55	177.39	218.50
T-0.06 (2)	1.79	72.02	171.71	214.26
T-0.15 (1)	1.53	152.26	67.71	212.02
T-0.15 (2)	1.31	151.27	55.67	207.52
T-0.30 (1)	0.06	6.67	20.74	32.64
T-0.30 (2)	0.06	6.73	21.77	34.85
F-0.01 (1)	2.35	7.08	181.33	212.62
F-0.01 (2)	2.34	7.11	182.23	213.10
F-0.06 (1)	1.98	11.96	162.99	194.18
F-0.06 (2)	1.96	11.90	161.38	192.08
F-0.15 (1)	1.94	31.01	151.62	202.21
F-0.15 (2)	1.91	30.71	150.19	199.99
F-0.30 (1)	0.76	109.00	19.54	142.23
F-0.30 (2)	1.21	102.00	19.30	169.41

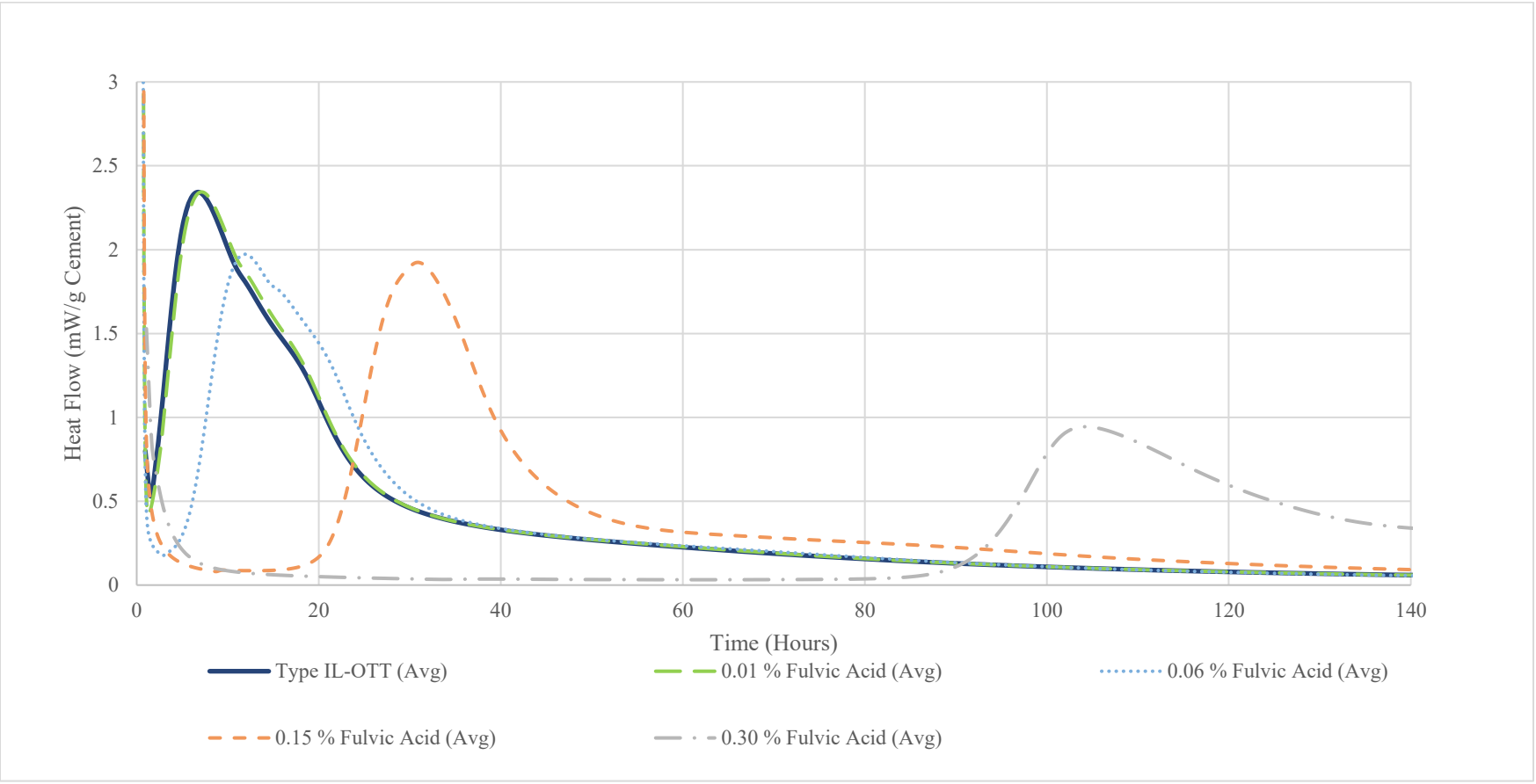

Figure B-1 Isothermal Calorimetry Conducted on ASTM C778 Standard Graded Sand and Controlled Additions of Fulvic Acid (Heat Flow)

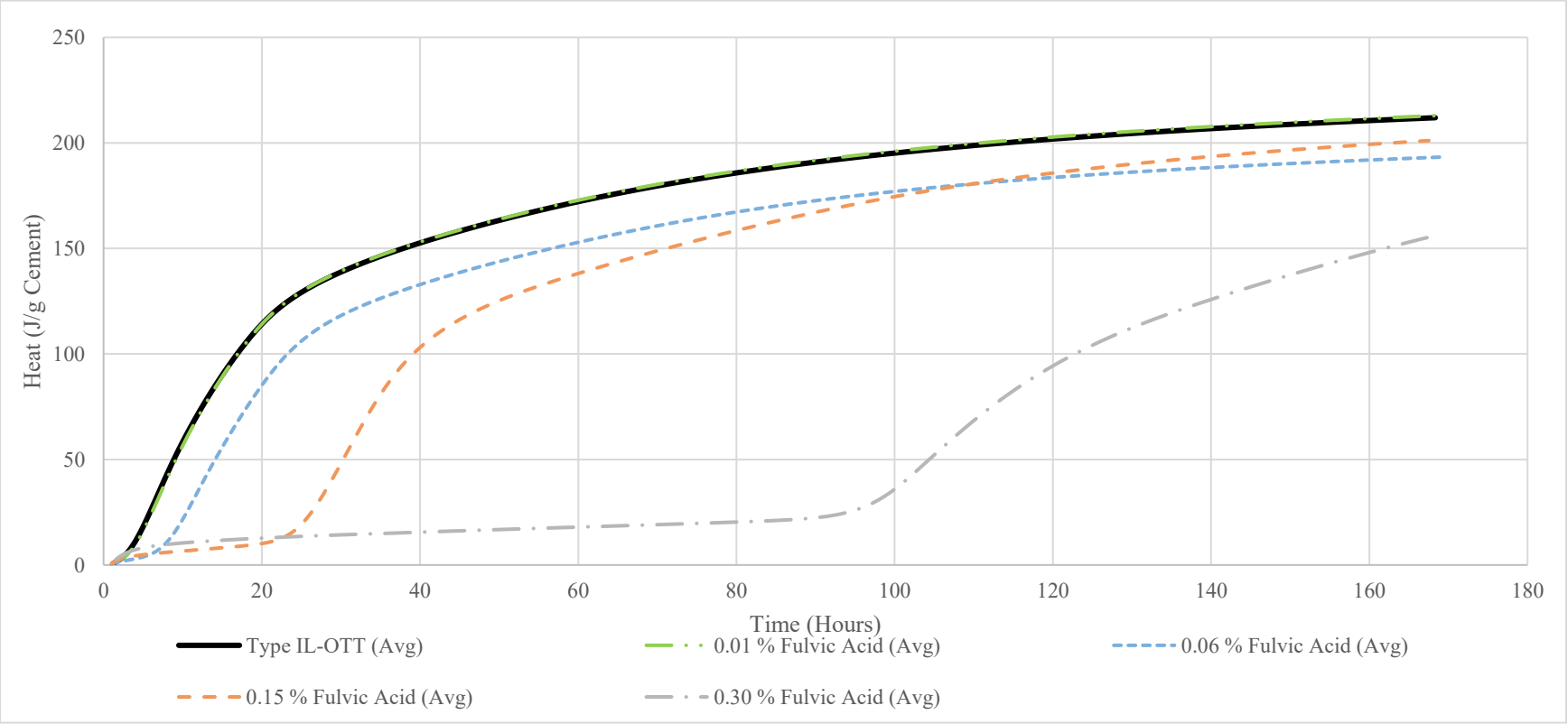

Figure B-2: Isothermal Calorimetry Conducted on ASTM C778 Standard Graded Sand and Controlled Additions of Fulvic Acid (Cumulative Heat)

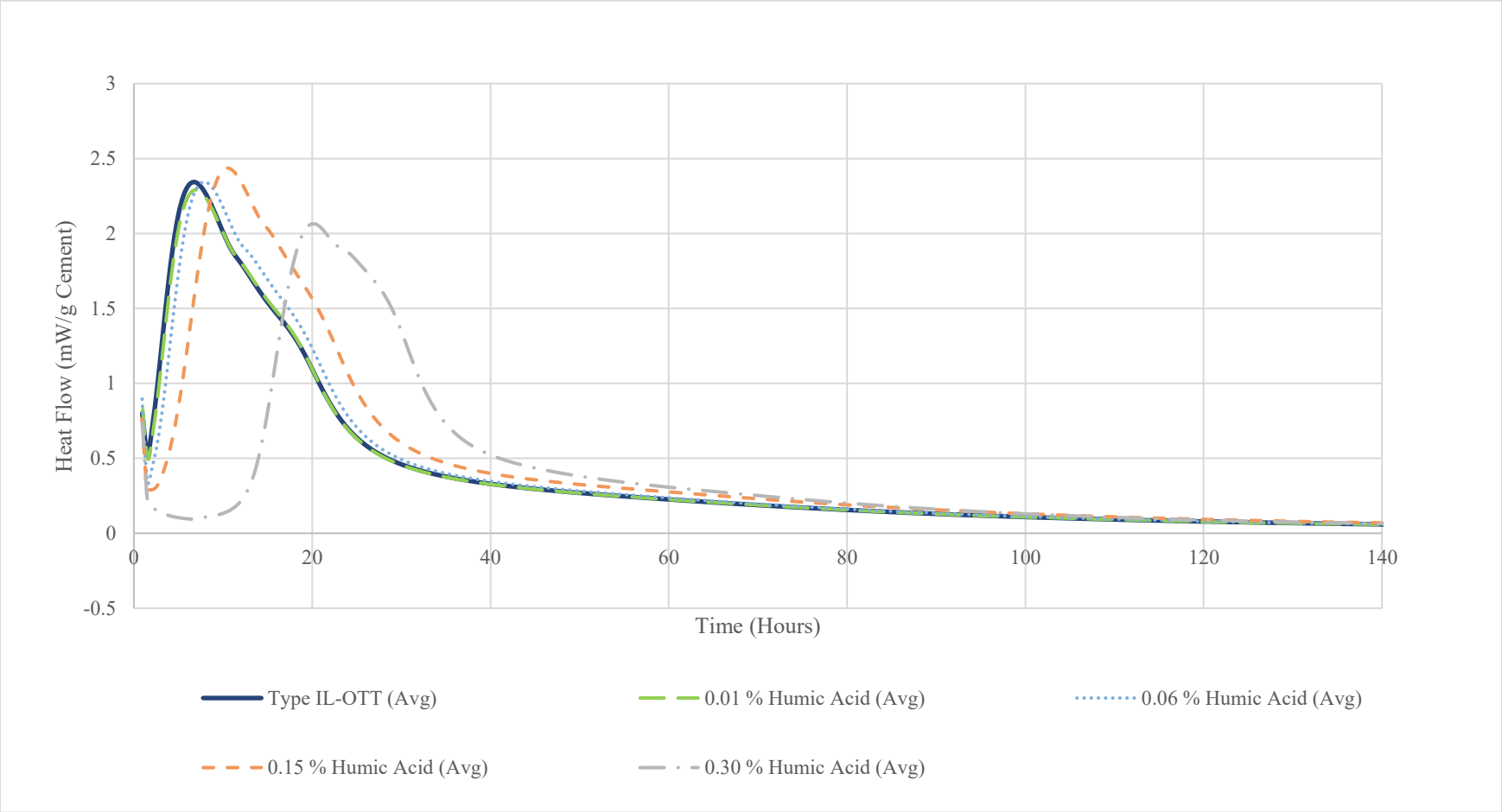

Figure B-3: Isothermal Calorimetry Conducted on ASTM C778 Standard Graded Sand and Controlled Additions of Humic Acid (Heat Flow)

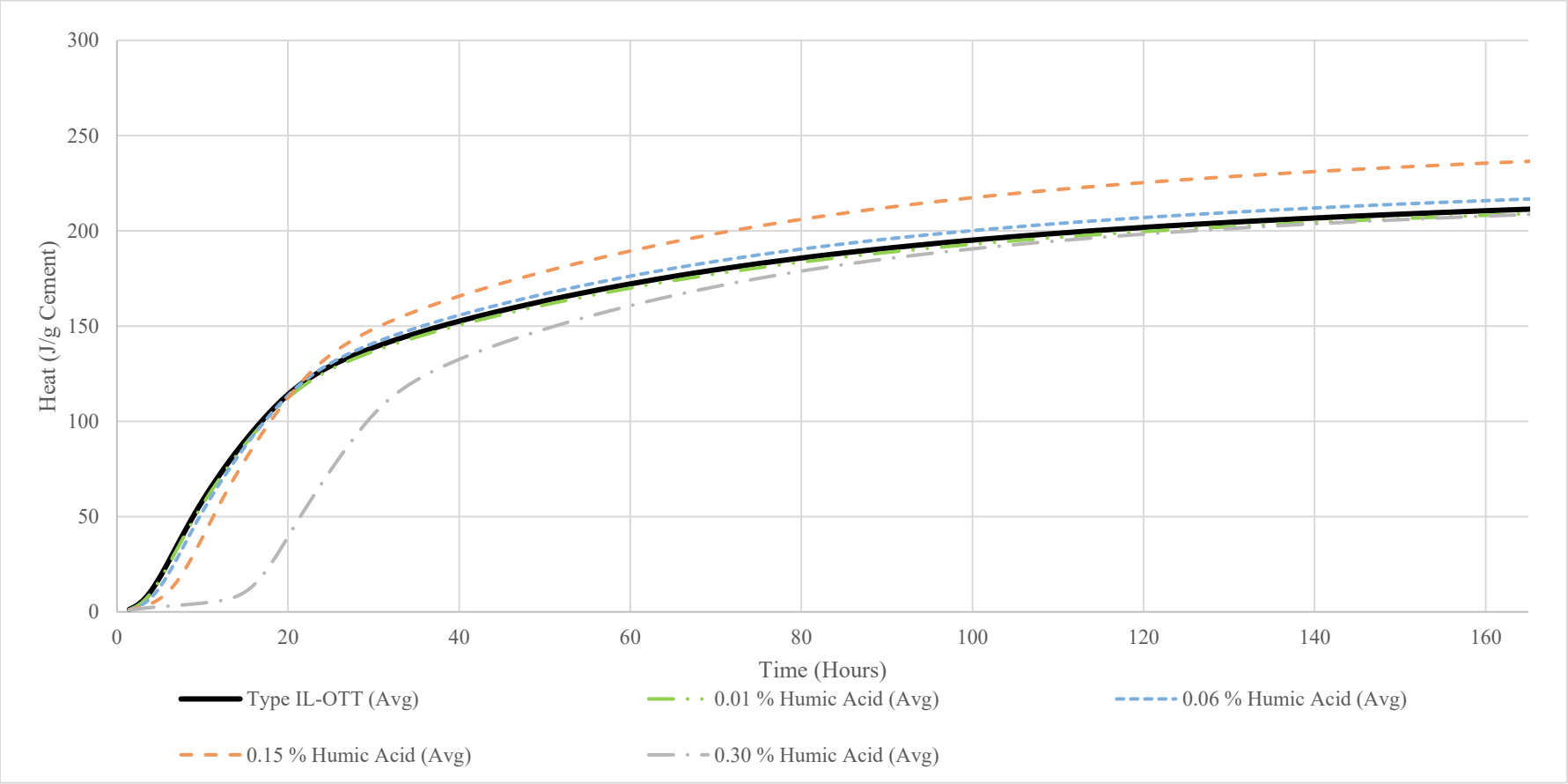

Figure B-4: Isothermal Calorimetry Conducted on ASTM C778 Standard Graded Sand and Controlled Additions of Humic Acid (Cumulative Heat)

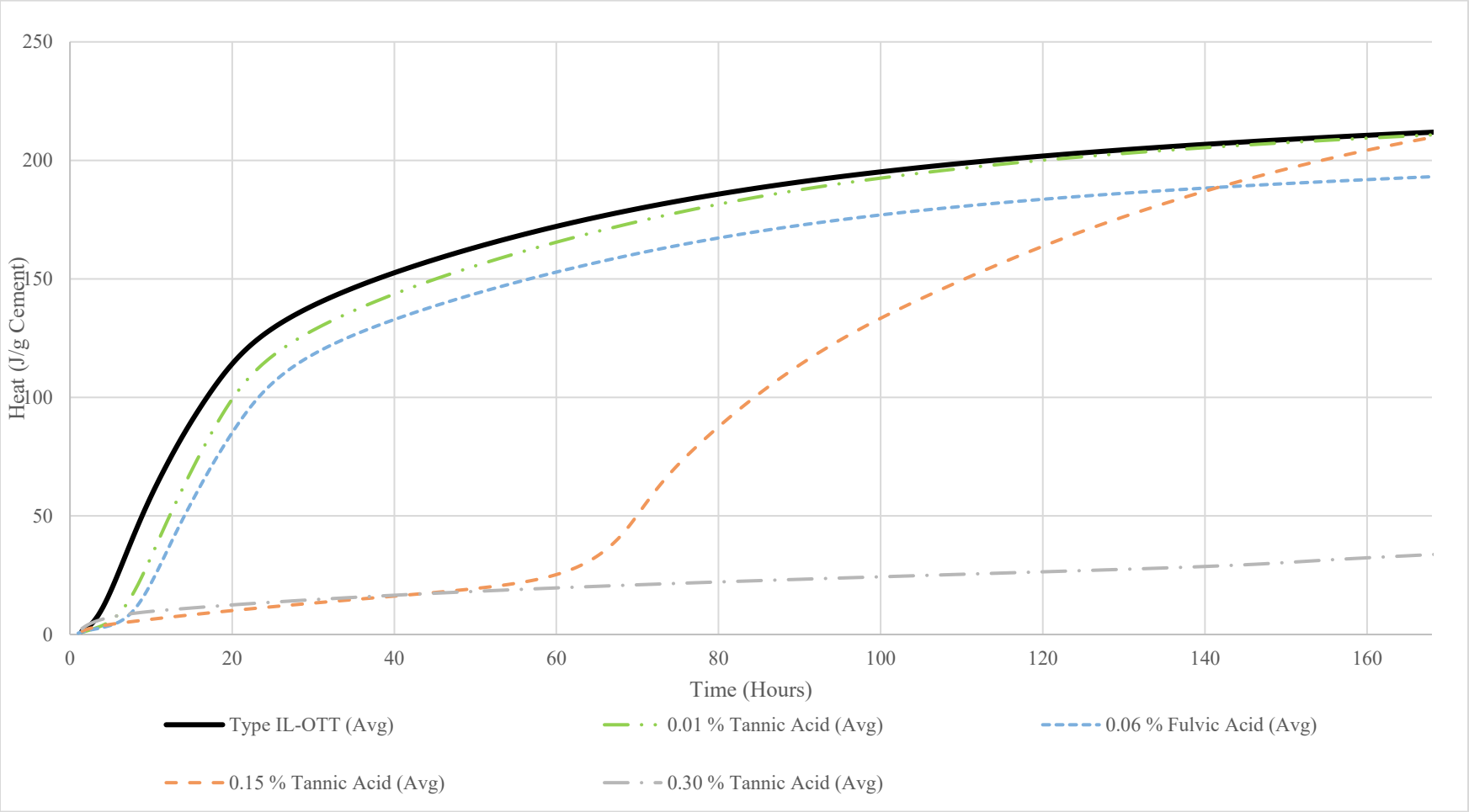

Figure B-5: Isothermal Calorimetry Conducted on ASTM C778 Standard Graded Sand and Controlled Additions of Tannic Acid (Cumulative Heat)

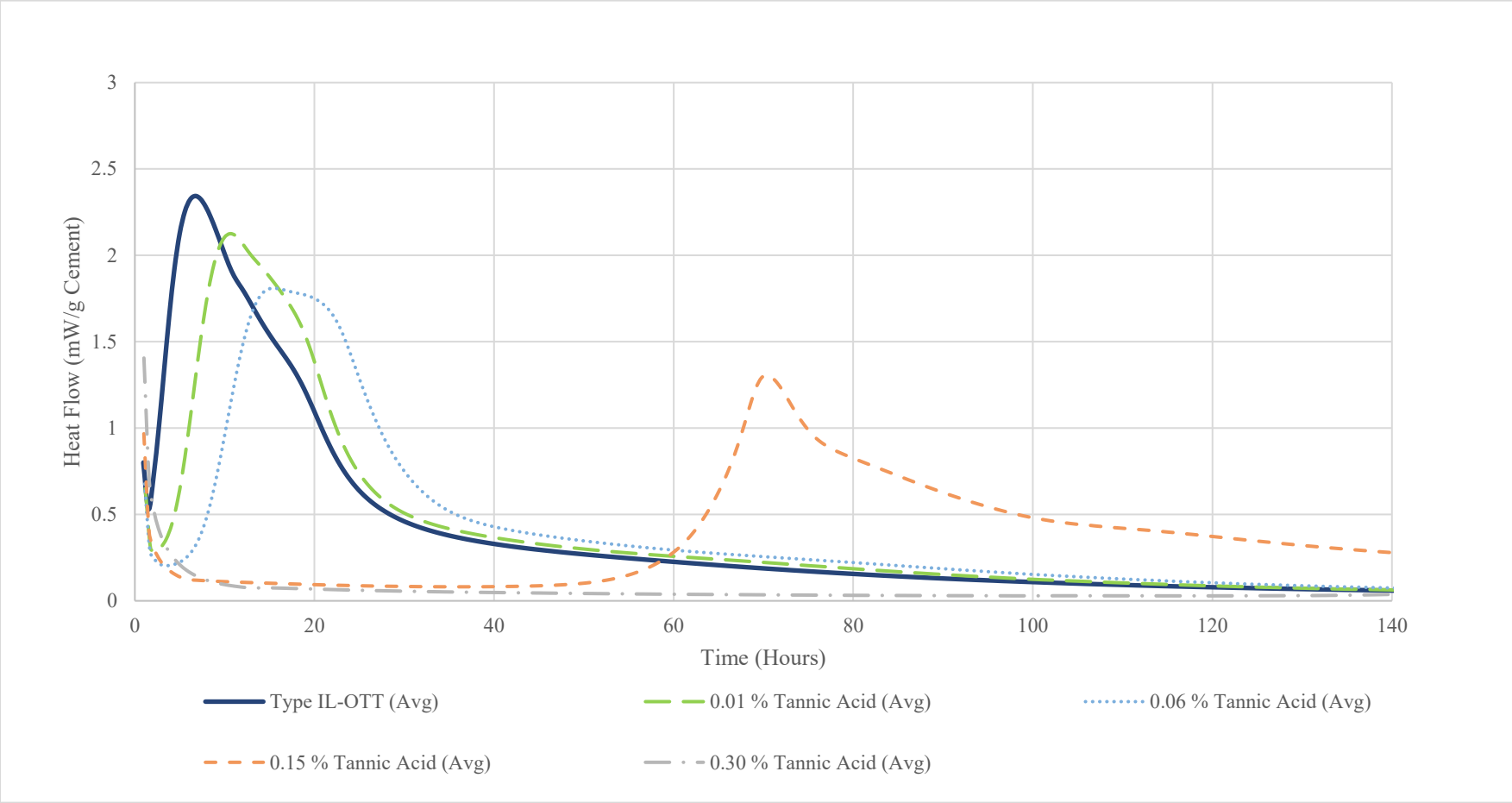

Figure B-6: Isothermal Calorimetry Conducted on ASTM C778 Standard Graded Sand and Controlled Additions of Tannic Acid (Heat Flow)

Table B-17: Data and ANOVA Results From Figure 4-48

Mine ID	Organic Carbon % via MWB	Main Calcium Silicate Peak Heat (mW/g)
C-0	0.00%	2.34
H-0.01	0.01%	2.29
H-0.06	0.02%	2.35
H-0.15	0.05%	2.44
H-0.3	0.10%	2.06
F-0.01	0.01%	2.34
F-0.06	0.03%	1.97
F-0.15	0.07%	1.93
F-0.3	0.14%	0.99
T-0.01	0.01%	2.14
T-0.06	0.03%	1.84
T-0.15	0.07%	1.42
T-0.3	0.16%	0.06
Multiple R	0.867743	
R Square	0.752979	
P- Value	0.000121	

Table B-18: Data and ANOVA Results From Figure 4-49

Mine ID	TOC% via MWB	Main Calcium Silicate Peak Time (h)
C-0	0.00%	6.61
H-0.01	0.01%	7.1
H-0.06	0.02%	11.93
H-0.15	0.05%	30.86
H-0.3	0.10%	105.5
F-0.01	0.01%	7.1
F-0.06	0.03%	11.93
F-0.15	0.07%	30.86
F-0.3	0.14%	105.5
T-0.01	0.01%	7.1
T-0.06	0.03%	11.93
T-0.15	0.07%	30.86
T-0.3	0.16%	105.5
Multiple R	0.933398	
R Square	0.871232	
P- Value	3.17E-06	

Table B-19: Data and ANOVA Results From Figure 4-50

Mine ID	Cumulative Heat (J/g) @ 72 hours	3-day strength (psi)
C-0	181.2	2450
H-0.01	179.12	1760
H-0.06	185.76	2180
H-0.15	199.84	2240
H-0.3	172.26	1500
F-0.01	181.78	1530
F-0.06	162.19	1500
F-0.15	150.91	0
F-0.3	19.42	0
T-0.01	175.92	2820
T-0.06	174.55	2390
T-0.15	61.69	300
T-0.3	21.255	0
Multiple R	0.814184	
R Square	0.662896	
P- Value	0.000704	

Table B-20: Data and ANOVA Results From Figure 4-51

Mine ID	Cumulative Heat (J/g) @ 168 hours	7-day strength (psi)
C-0	211.92	3100
H-0.01	209.57	3430
H-0.06	217.29	2770
H-0.15	236.78	2810
H-0.3	208.69	2340
F-0.01	212.86	3430
F-0.06	193.13	1940
F-0.15	201.1	1960
F-0.3	155.82	660
T-0.01	210.77	3430
T-0.06	216.38	3710
T-0.15	209.77	3080
T-0.3	33.75	0
Multiple R	0.834627	
R Square	0.696603	
P- Value	0.000387	

Table B-21: Data and ANOVA Results From Figure 4-52

Mine ID	Cumulative Heat (J/g) @ 168 hours	28-day strength (psi)
C-0	211.92	4330
H-0.01	209.57	4210
H-0.06	217.29	4250
H-0.15	236.78	4050
H-0.3	208.69	3150
F-0.01	212.86	4120
F-0.06	193.13	3150
F-0.15	201.1	2760
F-0.3	155.82	980
T-0.01	210.77	3790
T-0.06	216.38	3800
T-0.15	209.77	4340
T-0.3	33.75	0
Multiple R	0.89307	
R Square	0.797574	
P- Value	3.95E-05	

Table B-22: Data and ANOVA Results From Figure 4-54

Mine ID	TOC% via MWB	28-day strength (psi)
C-0	0.00%	4330
H-0.01	0.01%	4210
H-0.06	0.02%	4250
H-0.15	0.05%	4050
H-0.3	0.10%	3150
F-0.01	0.01%	4120
F-0.06	0.03%	3150
F-0.15	0.07%	2760
F-0.3	0.14%	980
T-0.01	0.01%	3790
T-0.06	0.03%	3800
T-0.15	0.07%	4340
T-0.3	0.16%	0
Multiple R	0.882313	
R Square	0.778476	
P- Value	6.55E-05	

Table B-23: Data and ANOVA Results From Figure 4-53

Mine ID	AASHTO T-21 Results	28-day strength (psi)
C-0	1	4330
H-0.01	3	4210
H-0.06	5	4250
H-0.15	5	4050
H-0.3	5	3150
F-0.01	1	4120
F-0.06	3	3150
F-0.15	4	2760
F-0.3	5	980
T-0.01	2	3790
T-0.06	4	3800
T-0.15	5	4340
T-0.3	5	0
Multiple R	0.407926289	
R Square	0.166403857	
P- Value	0.166453783	