



OKLAHOMA TRANSPORTATION CENTER

ECONOMIC ENHANCEMENT THROUGH INFRASTRUCTURE STEWARDSHIP

LASER CHARACTERIZATION OF FINE AGGREGATE

WARREN H. CHESNER, PH.D., P.E.
NANCY J. McMILLAN, PH.D., AOJN
STEPHEN A. CROSS, PH.D., P.E.

OTCREOS10.1-12-F

Oklahoma Transportation Center
2601 Liberty Parkway, Suite 110
Midwest City, Oklahoma 73110

Phone: 405.732.6580
Fax: 405.732.6586
www.oktc.org

DISCLAIMER

The contents of this report reflect the views of the authors, who are responsible for the facts and accuracy of the information presented herein. This document is disseminated under the sponsorship of the Department of Transportation University Transportation Centers Program, in the interest of information exchange. The U.S. Government assumes no liability for the contents thereof.

TECHNICAL REPORT DOCUMENTATION PAGE

1. REPORT NO. OTCREOS10.1-12-F	2. GOVERNMENT ACCESSION NO.	3. RECIPIENTS CATALOG NO.	
4. TITLE AND SUBTITLE Laser Characterization of Fine Aggregate		5. REPORT DATE December 2012	
		6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Warren H. Chesner, Nancy J. McMillan and Stephen A. Cross		8. PERFORMING ORGANIZATION REPORT	
9. PERFORMING ORGANIZATION NAME AND ADDRESS School of Civil & Environmental Engineering Oklahoma State University 207 Engineering South Stillwater, Oklahoma 74078		10. WORK UNIT NO.	
		11. CONTRACT OR GRANT NO. DTRT06-G-0016	
12. SPONSORING AGENCY NAME AND ADDRESS Oklahoma Transportation Center (Fiscal) 201 ATRC, Stillwater, OK 74078 (Technical) 2601 Liberty Parkway, Suite 110 Midwest City, OK 73110		13. TYPE OF REPORT AND PERIOD COVERED Final Jan. 2011 – Dec. 2012	
		14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES The research team consisted of members from Oklahoma State University, Chesner Engineering, P.C. and New Mexico State University. Matching funds for this project were provided by Chesner Engineering, P.C. from <i>NCHRP 150 Automated Laser Spectrographic Pattern Matching for Aggregate Identification</i> . University Transportation Center Program			
16. ABSTRACT <p>This report describes the results of a research effort to establish the feasibility of using a laser monitoring system to provide real-time data to characterize aggregate properties in a laboratory or field environment. This was accomplished by using the known physical, chemical and mechanical properties and aggregate criteria as defined by AASHTO and ASTM test methods and correlating these properties with spectral emission data induced by a laser in a process referred to as Laser Induced Breakdown Spectroscopy (LIBS).</p> <p>The authors believe that the success of this research in making such a correlation is based on two primary factors; 1) The laser ablation process can generate an emission with over 13,000 potential wavelengths, and these data provide a rich spectra that can be used to pattern match or fingerprint latent properties within the material that are not readily identifiable by conventional elemental or mineralogical testing methods, and 2) the development of multivariate statistical software models that can process large spectral arrays has made it possible to manage and analyze in real time data from the emission spectra generated during a laser ablation process.</p> <p>The primary advantage of LIBS over conventional aggregate testing and screening methods is its potential to identify the aggregate source in real-time in the field without sample preparation. This provides a means to identify preapproved materials and to ensure that only such materials are being introduced into the production process. It also provides a means to calibrate the spectral pattern or fingerprint against known engineering properties to determine whether the aggregate can be expected to pass or fail designated test criteria. A pooled fund study is currently under development to demonstrate the subject technology in the field, providing owner/agencies with a real time, recording tool for monitoring materials used in highway construction.</p>			
17. KEY WORDS laser induced breakdown spectroscopy, alkali-silica reactivity, aggregate identification, principal component analysis		18. DISTRIBUTION STATEMENT No restrictions. This publication is available at www.oktc.org and from the NTIS.	
19. SECURITY CLASSIF. (OF THIS REPORT) Unclassified	20. SECURITY CLASSIF. (OF THIS PAGE) Unclassified	21. NO. OF PAGES 58 + covers	22. PRICE

SI (METRIC) CONVERSION FACTORS

Approximate Conversions to SI Units				
Symbol	When you know	Multiply by	To Find	Symbol
LENGTH				
in	inches	25.40	millimeters	mm
ft	feet	0.3048	meters	m
yd	yards	0.9144	meters	m
mi	miles	1.609	kilometers	km
AREA				
in ²	square inches	645.2	square millimeters	mm ²
ft ²	square feet	0.0929	square meters	m ²
yd ²	square yards	0.8361	square meters	m ²
ac	acres	0.4047	hectares	ha
mi ²	square miles	2.590	square kilometers	km ²
VOLUME				
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft ³	cubic feet	0.0283	cubic meters	m ³
yd ³	cubic yards	0.7645	cubic meters	m ³
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.4536	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
TEMPERATURE (exact)				
°F	degrees Fahrenheit	(°F-32)/1.8	degrees Celsius	°C
FORCE and PRESSURE or STRESS				
lbf	poundforce	4.448	Newtons	N
lbf/in ²	poundforce per square inch	6.895	kilopascals	kPa

Approximate Conversions from SI Units				
Symbol	When you know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.0394	inches	in
m	meters	3.281	feet	ft
m	meters	1.094	yards	yd
km	kilometers	0.6214	miles	mi
AREA				
mm ²	square millimeters	0.00155	square inches	in ²
m ²	square meters	10.764	square feet	ft ²
m ²	square meters	1.196	square yards	yd ²
ha	hectares	2.471	acres	ac
km ²	square kilometers	0.3861	square miles	mi ²
VOLUME				
mL	milliliters	0.0338	fluid ounces	fl oz
L	liters	0.2642	gallons	gal
m ³	cubic meters	35.315	cubic feet	ft ³
m ³	cubic meters	1.308	cubic yards	yd ³
MASS				
g	grams	0.0353	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.1023	short tons (2000 lb)	T
TEMPERATURE (exact)				
°C	degrees Celsius	9/5+32	degrees Fahrenheit	°F
FORCE and PRESSURE or STRESS				
N	Newtons	0.2248	poundforce	lbf
kPa	kilopascals	0.1450	poundforce per square inch	lbf/in ²

ACKNOWLEDGEMENTS

Chesner Engineering, P.C. provided the match for this project from a project funded by the Transportation Research Board National Academies under the TRB-IDEA Program (NCHRP-150). Special thanks is extended by the Research Team to the TRB Project Director, Inam Jawed and the Advisory Panel: Georgene Geary, the Georgia Department of Transportation, William Skerritt, New York State Department of Transportation (NYSDOT), Randy Billinger, Kansas Department of Transportation (KSDOT), Caroline Herrera and Edward Morgan , Texas Department of Transportation (TXDOT), and Rosalie Multari, Applied Research Associates.

Three State transportation agencies (NYSDOT, KSDOT and TXDOT) and one contractor/material supplier (APAC-Central) participated in the research effort, supplying aggregate used in the laser test program and engineering test data from which the models presented herein were developed. A special thanks to William Skerritt, Randy Billinger, Ed Morgan, Michael Bailey and Ronnie Briusfield for providing data, interface and guidance relative to the nature of the materials being tested.

Additional members of the Research team who provided invaluable support throughout the effort included Carlos Montoya and Sandra Mader, New Mexico State University and Henry Justus, Chesner Engineering, P.C.

LASER CHARACTERIZATION OF FINE AGGREGATE

**Final Report
December 30, 2012**

**Warren C. Chesner, Ph.D., P.E.
Chesner Engineering, P.C.
Long Beach, NY**

**Nancy J. McMillan, Ph.D., AOJN
Professor & Academic Department Head
Department of Geological Sciences
New Mexico State University
Las Cruces, NM 88003**

**Stephen A. Cross, Ph.D., P.E.
Professor
School of Civil & Environmental Engineering
Oklahoma State University
Stillwater, OK 74078**

**Oklahoma Transportation Center
(Fiscal) 201 ATRC, Stillwater, OK 74078
(Technical) 2601 Liberty Parkway, Suite 110
Midwest City, OK 73110**

TABLE OF CONTENTS

EXECUTIVE SUMMARY	1
INTRODUCTION.....	6
Product.....	6
Report Content	7
Concept and Innovation	7
The Process.....	7
Multivariate Statistical Modeling.....	8
Laser Targeting and Spectrographic Equipment	10
Investigation	11
Research and Modeling Objectives.....	11
Sample Acquisition	12
LIBS Equipment.....	13
Sample Analysis	14
Multivariate Statistical Modeling	14
NEW YORK STATE: FRICTION AGGREGATES	16
Objectives and Analysis.....	16
Modeling Procedures: NYAIR Model-Acid Insoluble Residue	18
Modeling Results: NYAIR Model-Acid Insoluble Residue	18
Modeling Procedures: NYNCC Model - Percent Noncarbonate in Carbonate-Noncarbonate Blend.....	19
Modeling Results: NYNCC Model - Percent Noncarbonate in Carbonate-Noncarbonate Blend.....	20
State of Kansas: d-cracking AGGREGATES	21
Objectives and Analysis.....	21
Modeling Procedures: KSSBI Model-Source Bed Identification.....	23
Modeling Results: KSSBI Model-Source Bed Identification.....	28
Modeling Procedures: KSDPF Model – D-Cracking Pass/Fail Classification	29
Modeling Results: KSDPF Model – D-Cracking Pass/Fail Classification	30
State of Texas: alkali silica reactive AGGREGATES	31
Objectives and Analysis.....	31
Modeling Procedures: TXCQS Model – Chert Content in Quartz Sand	32
Modeling Results: TXCQS Model – Chert Content in Quartz Sand.....	32
Modeling Procedures: TXRC Model – Reactivity Classification	33
Modeling Results: TXRC Model – Reactivity Classification	35

Modeling Procedures: TXCSI Model - Chert Source Identification	35
Modeling Results: TXCSI - Chert Source Identification.....	40
APAC-CENTRAL: ANALYSIS OF FINE AGGREGATES	40
Objectives and Analysis.....	40
Modeling Procedures: APACC Model – Chert Content in Fine Sand	42
Modeling Results: APACC Model – Chert Content in Fine Sand	42
Modeling Procedures: APACF Model – Fe Content in Fine Sand	43
Modeling Procedures: OKF Model – Fe Content in Fine Sand	44
FINDINGS AND CONCLUSIONS	45
Plans for Implementation	46
REFERENCES.....	48

LIST OF FIGURES

Figure 1 Photon released in energy transition	2
Figure 2 LISB emission spectrum for TXDOT alkali silica reactive chert sample	2
Figure 3 Laser ablation process	3
Figure 4 Quality identification model	4
Figure 5 Product identification model	4
Figure 6 Spectra data output.....	8
Figure 7 Spectral data modeling objectives.....	9
Figure 8 Integrated LIBS system components	10
Figure 9 Examples of aggregates used in this study. Ruler is 6" long.....	13
Figure 10 LIBS lab system at New Mexico State University.....	14
Figure 11 Friction aggregate quality control procedures in New York	17
Figure 12 NYAIR calibration model for AIR content in NYSDOT carbonates	19
Figure 13 Calibration curve for percent noncarbonate rock in a noncarbonate-carbonate aggregate blend	21
Figure 14 PCA score plot for the 16 limestone beds used in the KSSBI Model	25
Figure 15 Model 1 PLS indicator integer regression in the KSSBI	25
Figure 16 KSSBI matching algorithm for identification of aggregate source beds.....	26
Figure 17 PCA score plot for Model 4 of KSSBI, in which the beds are separated into two groups.....	27
Figure 18 Results of Model 1 test-set validation.....	28
Figure 19 Model 12 subsample averaging (large circle and large triangle depict averages of subsamples resulting in 100% predictability).	30
Figure 20 Calibration and validation results for KSDPF model. The calibration model (top panel) results in 100% correct identification of the test-set spectra lower panel). ..	31
Figure 21 TXCQS calibration model for percent chert in a chert-quartz mixture	33
Figure 22 Calibration of TXRC model for classifying reactive and less-reactive chert types.....	34
Figure 23 Validation of TXRC model for classifying reactive and less-reactive chert types.....	35
Figure 24 PCA score plot for the 4 chert samples used in the TXCSI model	37
Figure 25 Model 1 PLS indicator integer regression in the TXCSI model.....	37
Figure 26 PCA score plot for the 3 remaining chert samples used in the TXCSI model	38
Figure 27 Model 2 PLS indicator integer regression in the TXCSI model.....	38
Figure 28 PCA score plot for the 2 remaining chert samples used in the TXCSI model	39
Figure 29 Model 3 PLS indicator integer regression in the TXCSI model.....	40
Figure 30 Matching algorithm model for TXDOT chert samples.....	41
Figure 31 Calibration of chert-quartz model and analysis of chert in Van Buren sand ..	43
Figure 32 Fe calibration for Muskogee sand	44

LIST OF TABLES

Table 1. Model Development	12
Table 2. Model Development Summary Table	15
Table 3. Ten NYSDOT AIR Calibration Samples	17
Table 4. Additional Eight NYSDOT Carbonate-Noncarbonate Calibration Samples	18
Table 5. Determination of Percent AIR in Two Carbonates.....	19
Table 6. Determination of Silicate Rock Content in Three Mixtures	21
of Traprock and a Moderate-Residue Limestone	21
Table 7. KSDOT Calibration and Validation Samples	23
Table 8. Success Rates for KSSBI Algorithm.....	29
Table 9. Results for Analyzed Mixtures of Chert and Quartz.....	33
Table 10. TXDOT Chert Samples Used in TXRC Model.....	34
Table 11. Mineralogy of the Van Buren Sand, From Point-Count Data	42
Table 12. Results of Chert Analysis in Van Buren Sands.....	43
Table 13. Fe Concentrations in Splits of Muskogee Sand.....	44
Table 14. Results of Fe Analysis, Muskogee Sand	45

EXECUTIVE SUMMARY

To ensure an uninterrupted supply of high quality aggregates for use in Portland cement, asphalt cement and unbound stone products, transportation agencies include test methods and criteria in their standard specifications to define the physical, chemical and mechanical property criteria that aggregates must exhibit for each specific end use. Most agencies rely on laboratory based test methods compiled by organizations such as the American Association of State and Highway Transportation Officials (AASHTO) and the American Society of Testing Materials (ASTM) to describe the appropriate test methods and criteria. Some of the more common aggregate properties supporting these specifications include gradation, specific gravity, absorption, organic content, plasticity, abrasion resistance, soundness, freeze thaw resistance, friable particles, insoluble residue, and aggregate reactivity. Almost all existing test methods and their corresponding criteria are empirical in nature and are based on studies undertaken over the years that have defined correlations between the results of laboratory test data and field experience.

Most AASHTO and ASTM test methods are laboratory-based, and require the collection of representative samples for subsequent transport to a laboratory for analysis. Turnaround times from sampling to the completion of testing vary widely depending on the test method, but can range from a few hours to a few days to several weeks and even several months. As a result, aggregate quality assurance is in great part dependent on the collection, testing, and preapproval of aggregate sources prior to the actual material production process. Many agency quality assurance plans require that additional samples be collected during the production process to verify that the actual aggregate employed during production matches the preapproved sources. Unfortunately, when such methods are employed, the pavement or concrete structure is typically in-place by the time tests results become available. In certain instances, failure of such verification to comply with the appropriate specification necessitates the removal and replacement of the newly installed structure.

This report describes the results of a research effort to establish the feasibility of using a laser monitoring system to provide real-time data to characterize aggregate properties in a laboratory or field environment. The approach does not employ new engineering test methods. It makes use of the known physical, chemical and mechanical properties and aggregate criteria as defined by AASHTO and ASTM, and correlates these properties with spectral emission data induced by a laser in a process referred to as Laser Induced Breakdown Spectroscopy (LIBS). To gain greater insight into this technology requires an overview of the process of atomic emission or optical emission spectroscopy and multivariate statistical modeling.

Atomic emission spectroscopy (AES) is a spectroscopic technique that examines the wavelengths of photons emitted by atoms or molecules of a sample material during their transition from an excited state to a lower energy state (see Figure 1). Each element emits a characteristic set of discrete wavelengths according to its electronic structure. By observing these wavelengths and their respective emission intensities, the elemental

composition of the sample can be determined (see Figure 2.) For example, if an element, such as sodium, is known to emit at a certain wavelength, then the intensity of the light emitted at that wavelength can be used to determine the sodium concentration in the sample.

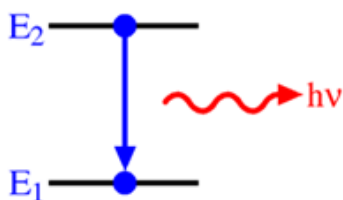


Figure 1 Photon released in energy transition.

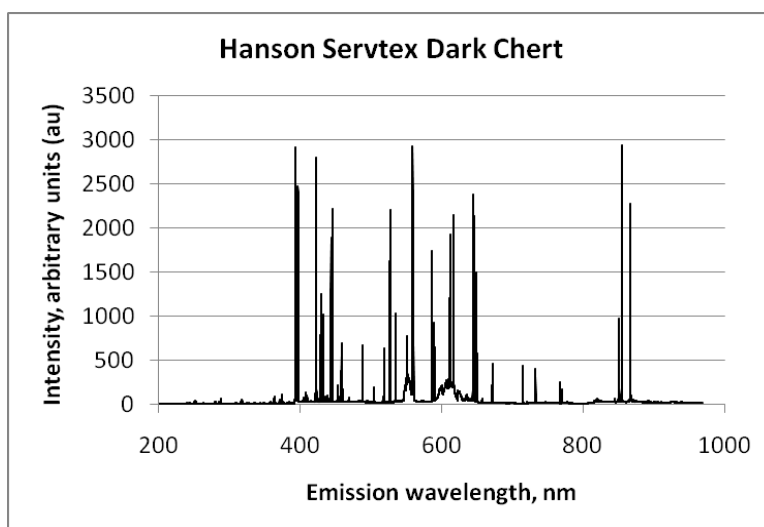


Figure 2 LISB emission spectrum for TXDOT alkali silica reactive chert sample.

There are many ways in which atoms can be brought to an excited state. The simplest method is to heat the sample with a flame to a high temperature. Electrical discharges such as arcs and sparks can provide the necessary energy as well as high-powered lasers, which can induce high energy plasmas. High powered lasers can impart much greater energy than flame or electrical excitation sources, causing the electrons to populate higher energy levels resulting in spectra with many more energy lines. This process is accomplished by focusing a laser onto a very tiny spot on a target material achieving a very high irradiance. During plasma formation (see Figure 3), electrons interact and subsequently, within microseconds, recombine with ions to release energy

across a broad spectral range. Flame or electrically induced AES is almost exclusively used in a laboratory environment where its primary purpose is to determine elemental concentrations of the target sample. A laser, however, can be employed as a remote sensing instrument designed to operate without sample preparation and in a field environment.

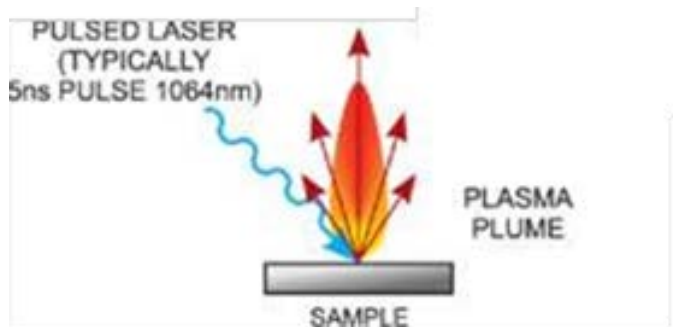


Figure 3 Laser ablation process.

The subject technology (LIBS) has the potential to be employed as an automatic laser monitoring system to provide real-time data of aggregate quality in a field environment. Unlike AES however, the objective is not to determine the elemental concentration of the target sample or aggregate. Instead, it is intended as a means to generate a spectral pattern, defined not by one wavelength, but by the interrelationship or pattern associated with over 13,000 different wavelengths. Analyzing a spectral output containing over 13,000 different wavelengths to define specific patterns cannot be done using traditional data analysis techniques. Multivariate discriminant analysis provides the means to simultaneously analyze multivariate data [1], and provide the means to correlate spectral patterns with and defined engineering properties. Using multivariate statistical modeling techniques, such patterns, which provide information on the latent properties of the aggregate material, have the potential to discriminate between aggregate types and identify specific aggregate properties. Discriminant modeling can be used as an indicator of whether the spectrum of unknown samples matches the spectra from samples taken previously (a training or calibration set of samples) that were known to be either good or bad quality or to possess certain fundamental properties. Two illustrative examples are presented below in Figure 4 and Figure 5.

In Figure 4, the spectrum of an unknown sample is compared against the model to determine if it matches the training data for the model. If the training set was constructed from spectra of samples that were of known quality, the model can accurately predict if the sample is of the same quality by matching the spectrum and giving a "yes" or "no" answer. In Figure 5, the spectrum of the sample is compared to multiple training models of different materials or different levels of quality of the same

material. The models can predict the likelihood that an unknown sample matches the training spectra they were constructed from, again giving a "yes" or "no" answer.

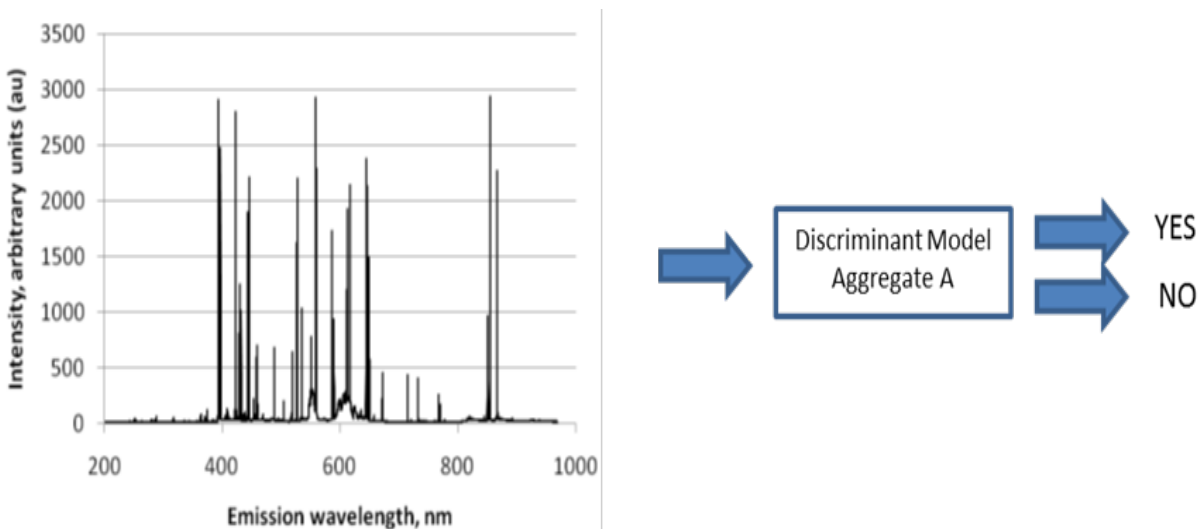


Figure 4 Quality identification model.

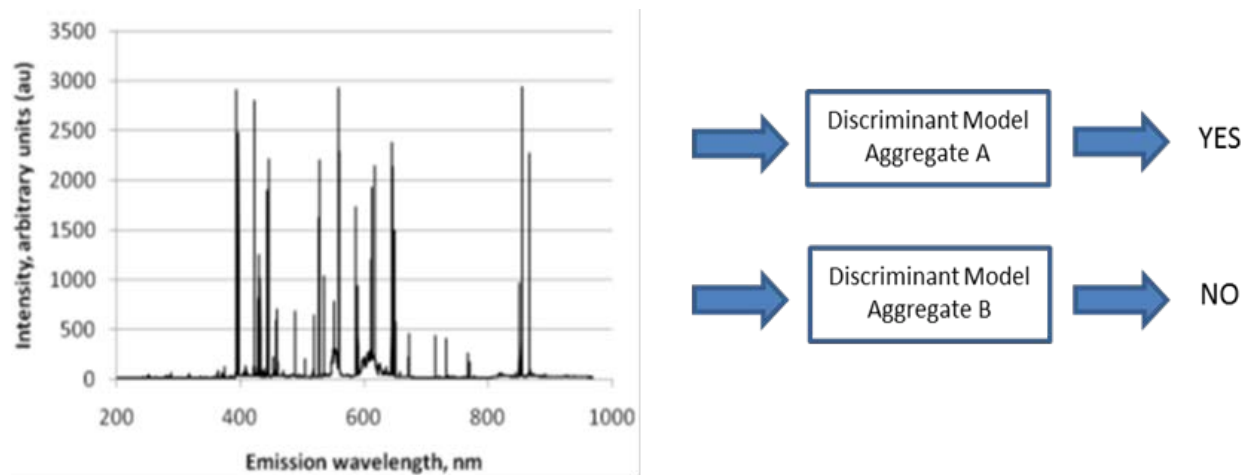


Figure 5 Product identification model.

Three State DOTs, New York State (NYSDOT), Kansas (KSDOT), and Texas (TXDOT) and one contractor/material supplier (APAC-Central) participated in the research effort to demonstrate the subject technology. Each supplied specific aggregates for laser calibration testing to determine if the technology could be used to identify specific aggregate types or engineering properties of interest, and to assess whether LIBS could

be used as a means to differentiate between good and poor aggregates as defined by the respective State specification criteria.

New York: Aggregates from New York were studied to see if the acid insoluble residue (AIR) content of carbonates (a test criteria used by NYSDOT to determine friction course acceptability) could be modeled, and whether a compositional blend of noncarbonated rocks, which are almost entirely composed of quartz or silicate minerals, mixed with limestone could be quantified (i.e., the percent noncarbonate rock in the blend).

Kansas: Aggregates from Kansas were examined to see whether the original (source) bed in a quarry, from which an unknown aggregate sample was extracted, could be identified by modeling the characteristics of the aggregate from each bed. D-cracking susceptible aggregates from Kansas were also analyzed to determine if models could be developed to discriminate between aggregates that passed and failed KSDOT D-cracking test criteria.

Texas: Aggregates from Texas were examined to determine if a compositional blend of chert and quartz sand could be quantified (i.e., the percent chert in the blend), whether high and low reactive cherts could be classified, and whether four cherts with different degrees of alkali silica reactivity (ASR) could be differentiated.

APAC-Central: Fine aggregates dredged from the Arkansas River in Arkansas (Van Buren sand) and Oklahoma (Muskogee sand) were analyzed for percent chert and weight percent iron (Fe), respectively.

The results of these studies were quite remarkable. In all cases, models were developed that were capable of identifying with a high degree of accuracy the quality of the test aggregate. For example, using the known AIR content of a series of carbonates from New York, it was possible to establish a highly accurate calibration model for estimating the acid insoluble residue (AIR) content of New York carbonate aggregates, and to use the model to predict the AIR content of test samples. It was possible to determine the compositional blend of noncarbonate rock in a noncarbonate-limestone blend. It was possible to model 16 beds from three Kansas quarries, and to identify the specific source bed of an unknown aggregate, and to model aggregates that pass or fail KSDOT tests for D-cracking aggregates. The analysis of alkali-silica reactive cherts received from TXDOT yielded similar, positive results as well. It was possible to differentiate between four types of chert, classify cherts as more or less reactive and develop a calibration curve to identify and quantify the percentage of reactive chert in quartz-chert mixtures. The chert calibration model, developed for TXDOT, was applied to chert in the Van Buren sand from Oklahoma, with errors of about 2%. Finally, the weight percent Fe was analyzed in Muskogee sand to within 0.08%.

The results of this research suggest that multivariate discriminant modeling of laser induced spectra can be used to correlate spectral output data with aggregate types and aggregate properties. This should not be surprising, since it is reasonable to assume

that the engineering properties (physical, chemical and mechanical) of aggregates, as defined by AASHTO and ASTM test criteria, are dependent in great part on the chemical and mineralogical nature of the aggregate material. On the other hand, while such an assumption is reasonable, it is noteworthy that few studies have (up until now) effectively developed correlating relationships between the chemical or mineralogical properties of aggregate materials with most engineering properties.

The authors believe that the success of this research in making such a correlation is based on two primary factors:

1. The laser ablation process can generate an emission with over 13,000 potential wavelengths, and these data provide a rich spectra that can be used to pattern match or fingerprint latent properties within the material that are not readily identifiable by conventional elemental or mineralogical testing methods.
2. The development of multivariate statistical software models over the past 20 to 30 years that can process large spectral arrays has made it possible to manage and analyze in real time data from the emission spectra generated during a laser ablation process.

In summary, the authors believe that the large data base along with the capability to model the data provide the framework for the predictive capability of the technology, in effect uncovering the latent properties present in the light emitted from the targeted aggregate material. The primary advantage of the subject technology over conventional aggregate testing and screening methods is its potential to identify the aggregate source in real-time in the field without sample preparation. This provides a means to identify preapproved materials and to ensure that only such materials are being introduced into the production process. It also provides a means to calibrate the spectral pattern or fingerprint against known engineering properties to determine whether the aggregate can be expected to pass or fail designated test criteria. Development and demonstration of the subject technology in the field could provide State DOTs and material suppliers with a real time, nearly instantaneous recording tool to address the need for transportation infrastructure material quality control monitoring.

INTRODUCTION

Product

The product under development is an automated real-time quality control aggregate monitoring system. The system employs a laser and supporting optical equipment to scan aggregates and provide real-time monitoring during the pavement production or aggregate mining process to screen materials without sample preparation. This provides a means to identify pre-approved materials, to ensure that only such materials are being introduced into the production process. It also provides a means to calibrate the fingerprint against known engineering properties to determine whether the aggregate can be expected to pass or fail designated test criteria. Successful deployment of such a system can provide a layer of quality control that the industry

currently does not have, thereby ensuring that the transportation infrastructure is being rehabilitated or constructed using quality materials that maximize service life.

Report Content

The remainder of this report is divided into the following sections. The first section, Concept and Innovation, describes the principles and technical basis of the laser aggregate monitoring system. The second section, Investigation, summarizes the aggregate types received from NYSDOT, KSDOT, TXDOT and APAC-Central for testing, the laser equipment, analytical procedures, data processing and general modeling approach utilized in the research effort. This section is followed by four sections that respectively focus on the source materials, testing methods, modeling methods and results of the NYSDOT, KSDOT, TXDOT and APAC-Central efforts. These specific sections are followed by the Findings and Conclusions section, which provides a concise listing of the major findings and conclusions of the research effort. The last section, Plans for Implementation, provides a description of the requirements for transitioning the technology from the laboratory to the field and developing plans for implementing this transition.

CONCEPT AND INNOVATION

The Process

The subject technology employs a rapid laser-scanning technique in which a very short-duration pulse of energy from a high-power laser is optically focused at a point, instantaneously heating the target sample to cause vaporization and atomization of nanograms of material within a microplasma. Because of the high plasma temperature (initially >8000 deg K), atoms and ions are electronically excited and upon return to ground state emit light across a broad spectral range (most importantly the range of 200 to 980 nm). The light generated by the plasma is characteristic of the chemical makeup of the ablated material. This light (emission) can be quantified by collecting it and generating a spectral image, which identifies the emission wavelengths and respective intensities in a spectrometer. The image is projected onto a charged couple detector. The spectral image can then be visually and mathematically recorded in a computer. Once the emission spectra are recorded and stored it is possible to make use of multivariate statistical techniques to generate models to profile or pattern match the spectral signal from unknown aggregate samples generated during the laser ablation process for comparison with spectra from known sources. This laser induced plasma or laser ablation process in which an emission spectra is captured is referred to as Laser Induced Breakdown Spectroscopy (LIBS).

The LIBS process is fundamentally similar to traditional atomic emission spectroscopic (AES) methods that are used for elemental analysis. Each element emits a characteristic set of discrete wavelengths according to its electronic structure. By observing these wavelengths and their respective emission intensities, the elemental composition of the sample can be determined (see Figure 2). Unlike traditional methods however, lasers have the unique advantage of providing real-time “remote sensing” capability in field applications. In addition, in the subject application the objective is not

to determine the elemental composition of the target sample. The objective is to model the emission spectral output generated during the laser ablation process. No one specific element makes up the model. It is a composite of the relationship of over 13,000 wavelengths of data.

Imbedded in the spectral output of a laser ablated sample is an enormous amount of data. These data provide information on the latent properties of the target material. If the data could be manipulated or modeled in such a way so as to reveal specific properties of interest, then the proposed pattern identification approach can be converted to a powerful analytical tool. This is in essence how the process works.

A schematic representation of the quantity of data imbedded in a spectral output is shown in the matrix presented in Figure 6. Each laser shot (1,2,3,4....s) shown on the left side of the matrix generates over 13,000 wavelengths or energy line outputs ($w_1, w_2, w_3, w_4, \dots, w_n$). Since lasers can be set to fire at frequencies ranging from 1 to 50 Hz, a very large sample population (s) can be generated. For example, the matrix shown in Figure 6 depicts a total of s shots and n energy lines. A laser firing at one shot per second (1 Hz) would generate 60 spectral outputs in one minute. At 10 shots per second (10Hz), 600 spectral outputs would be produced. The combination of the emission spectra with over 13,000 data points (i.e., variables) and the number of laser shots (i.e., samples) provide the means to generate models with unprecedented levels of information. These models, discussed in greater detail below, are capable of developing identifiable correlations with specific engineering properties or specific aggregate types.

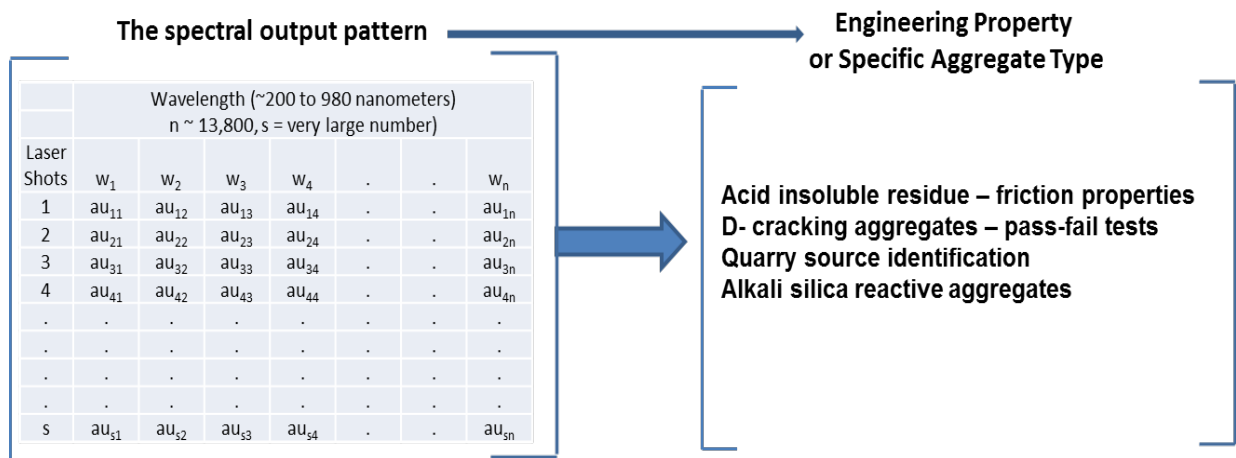


Figure 6 Spectra data output.

Multivariate Statistical Modeling

The collection of large numbers of measurements made on many samples has traditionally been analyzed using one or two variables at a time. This approach however cannot readily discover the relationships among all samples and variables efficiently. To

do this, all of the data must be processed simultaneously. Chemometrics is the field of extracting information from multivariate chemical data using tools of statistics and mathematics. This is directly applicable to laser induced spectral data, which can contain large numbers of samples and signals.

Multivariate modeling of chemical data can be used for three primary purposes:

1. To explore patterns of association in data,
2. To prepare and use multivariate classification or discriminant models, and
3. To track properties of materials on a continuous basis.

In the course of this investigation, all three purposes were applied. Using Principal Components Analysis (PCA) patterns of data were explored. Using Partial Least Squares Regression (PLS) Modeling, discriminant predictive models were prepared and finally, the data was used to initiate the development of a system to track properties of aggregate materials on a continuous basis.

Principal Components Analysis (PCA) and Partial Least Squares Regression (PLS) analysis are referred to as projection models. They use linear algebraic techniques on arrays of large samples of data, as shown in Figure 6, to generate new data projections. The new projections reduce the number of dimensions in the data so that relationships amongst the most important variables, if they exist, can be visualized and quantified. PCA in particular, permits an analyst to visualize whether the properties of samples introduced into the model can be differentiated. If the samples can be differentiated then this suggests that the structure of the data can be further analyzed to define underlying factors associated with the differences between the samples. Given these differences, PLS can then be used to develop predictive models that can correlate a multivariate array of independent variables, as depicted in the spectral data presented in Figure 6, to a dependent array of data. This is conceptually presented in Figure 7. The goal is to transpose the X-matrix (independent variables), which can represent the spectral output shown in Figure 6, into a new Y matrix (dependent variables) with fewer dimensions. In our case the goal is to reduce the X-matrix to a predictive Y-matrix that can be correlated with an aggregate type or property of interest. The models in this investigation were developed using PLS analysis. The specific properties listed in Figure 6 represent the actual properties that were modeled in this effort using aggregates from New York, Kansas and Texas.

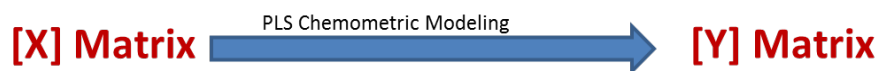


Figure 7 Spectral data modeling objectives

The predictive reliability of a multivariate model is dependent on the development of an effective calibration or training model that is subsequently used as the predictive model. The accuracy of such a model is dependent on the source of data used to

calibrate the model. If the sources are correctly selected, the more input data that are available the more reliable the model. The development of PLS models to predict aggregate properties from laser generated spectra can be designed to make use of an extremely large database. The size of these databases is unprecedented, insofar as engineering modeling applications are concerned. The number of samples and the number of variables that can be included in the calibration or training models provides the means to generate engineering property predictive tools that previously were not possible.

Laser Targeting and Spectrographic Equipment

The spectral output data used to develop input to the PLS models was acquired by Laser Induced Breakdown Spectroscopy (LIBS). A LIBS setup consists of a laser, mirrors and focusing lenses to focus the laser on the target sample. It includes collection lenses and optical fibers to collect and transmit the light generated by the ablation process to a spectrometer and a charged couple device (CCD) capable of recording and storing the data in a computer. A schematic showing a general equipment arrangement is shown in Figure 8.

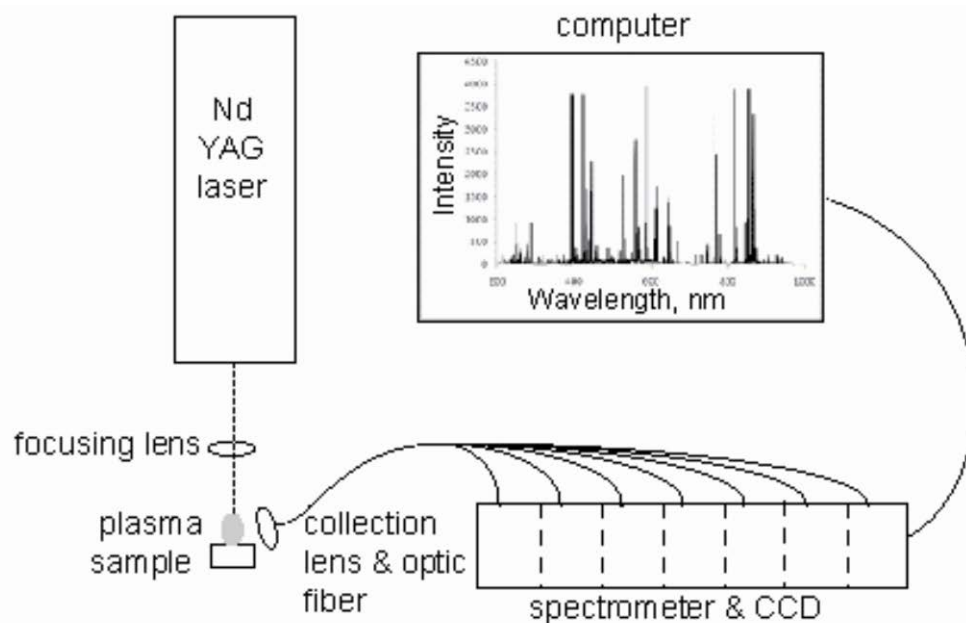


Figure 8 Integrated LIBS system components.

LIBS has been applied in a variety of applications since the late 1980s [2]. Some of these include coal and flue gas characterization, toxic material identification, explosives and chemical and biological weapons detection, soils analysis, and food quality. Major advances in the use of LIBS to identify geo-materials has been occurring [3,4,5] in great part due to a NASA Mars 2012 mission, where LIBS technology will be employed as part of the Mars rover to analyze Martian soils [6]. In 2003, the technology was proposed in Germany as a means to provide quality control on recycled concrete

aggregate [7]. The similarity of geo-materials to aggregate materials would appear to make the technology well suited for highway aggregate characterization, although no reported use of LIBS for quality control of virgin aggregate materials has been reported in the literature.

The integrated LIBS system depicted in Figure 8 is applicable to both a laboratory and a field monitoring system. Laboratory LIBS systems are currently available and can be purchased from vendors. The system used in this investigation is described in the next section. Few LIBS field systems however, have been developed for remote monitoring, and those that have been developed operate by preselecting a target material ablation point and focusing the laser on that location to generate a spectra that can be captured. If a second target shot is warranted, the laser must be repositioned and focused on the second target location. For aggregate (bulk material) field monitoring, such step by step laser focusing systems is not an ideal operational mode. In bulk monitoring, the full analytical power of LIBS and multivariate modeling can be better exploited by deploying a system where the laser can fired repeatedly at the target material analyzing numerous samples in a continuous manner. The authors have developed a patent pending system for such a purpose, which is described in the Plans for Implementation section of this report.

INVESTIGATION

Research and Modeling Objectives

The NYSDOT research focused on the feasibility of using LIBS spectra to develop models to predict the acid insoluble residue (AIR) content present in carbonate samples, as well as the quantity of silicate rock present in a silicate rock-carbonate (limestone) blend. Acid insoluble residue content is the primary friction-related test criteria used by NYSDOT to evaluate the acceptability of surface course aggregates.

The KSDOT research had two objectives. The first focused on the feasibility of using LIBS spectra to model aggregates from 16 beds in three quarries to predict whether the source bed of an unknown aggregate could be identified. The second focused on the feasibility of using LIBS spectra to model D-cracking susceptible aggregates to determine if D-Cracking pass/fail tests as specified by KSDOT could be predicted.

The TXDOT research focused on the use of LIBS spectra to develop models to predict the presence and percentage of an alkali silica reactive chert in a sample of nonreactive quartz sand, to classify chert as a high or low ASR reactive chert, and to identify specific chert types from a series of unknown samples.

The APAC-Central research focused on testing fine aggregates. The Van Buren sample was used to determine if the calibration model developed with TXDOT materials could accurately identify percent chert in the Van Buren sand. For the Muskogee sand, the research approach was to predict the amount of iron (Fe) present.

To undertake this effort, a total of nine separate models were developed. These are listed in Table 1.

Table 1. Model Development

Agency	Model
NYSDOT	Acid Insoluble Residue Calibration
NYSDOT	Noncarbonate Rock-Carbonate Blend Calibration
KSDOT	Quarry Bed Identification
KSDOT	D-Cracking Pass/Fail Test
TXDOT	Alkali-Silica Reactive Chert-Quartz Calibration
TXDOT	More reactive/Less reactive Chert
TXDOT	Chert Source Identification
APAC	Chert in Van Buren sand
APAC	Fe in Muskogee sand

The NYSDOT models that were developed were compositional (or calibration) models, in which the spectra were correlated to a known concentration of one or more selected variable. In New York, these variables were the percent acid insoluble residue in a carbonate aggregate, and the percent noncarbonate aggregate in a mixed noncarbonate-carbonate aggregate blend. The Kansas models were not compositional models. The identification of the source of an aggregate derived from one of 16 beds required the development of a matching algorithmic process that was designed to compare and match beds to one another in order to select the correct source bed. Pass-fail models used in Kansas' D-cracking studies were made using integer indicator variables that were regressed against spectra derived from aggregate that passed or failed the KSDOT D-cracking tests. TXDOT calibration models were a combination of calibration, integer indicator and matching algorithm models. In all cases, the models were tested with two separate sample sets: a calibration or training set and a validation set that were not included in model development. More descriptive details of these models are presented in subsequent sections where the models are applied. Both APAC models were compositional models.

Sample Acquisition

Aggregate samples, shown in Figure 9, were submitted by NYSDOT, KSDOT, TXDOT and APAC-Central in gallon-sized containers for testing. Particle sizes ranged from approximately ¼" to ½" in diameter; the TXDOT chert-quartz and APAC-Central samples were sand-sized. Detailed lists of the samples used in this research effort are presented in each respective section. NYSDOT provided carbonate samples with laboratory measured AIR values, in addition to various silicate aggregates. KSDOT provided samples from 16 limestone beds in three quarries from eastern Kansas, all of which were tested for D-cracking susceptibility. TXDOT provided samples of hand-picked reactive chert from several sources and pure non-reactive quartz sand. Samples received by the research team were rinsed in distilled, deionized water to remove dust and air-dried prior to testing. Two sands were submitted by APAC-Central for analysis in

5-gallon-sized containers. The Van Buren sand was tested for chert content and the Muskogee sand for Fe content.

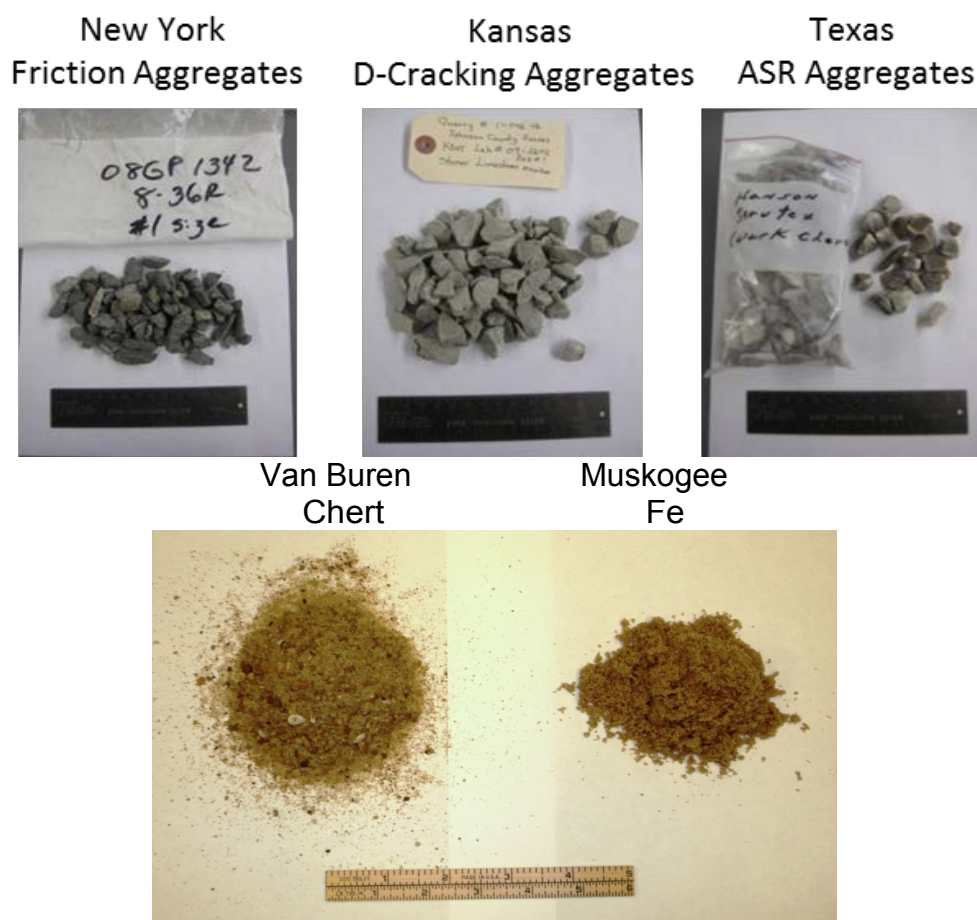


Figure 9 Examples of aggregates used in this study. Ruler is 6" long.

LIBS Equipment

The LIBS system used to generate and record the spectra consisted of an Nd:YAG 1064 nm 200 mJ laser supplied by Big Sky Laser Technologies, Inc., and an Ocean Optics LIBS 2500-7 channel system spectrometer. The laser system includes a sample chamber consisting of a sample platform, a focusing lens and a fiber optic cable designed to collect and transmit the light emission from the ablated aggregate to the spectrometer and charged couple device. A photograph of the LIBS system is shown in Figure 10.

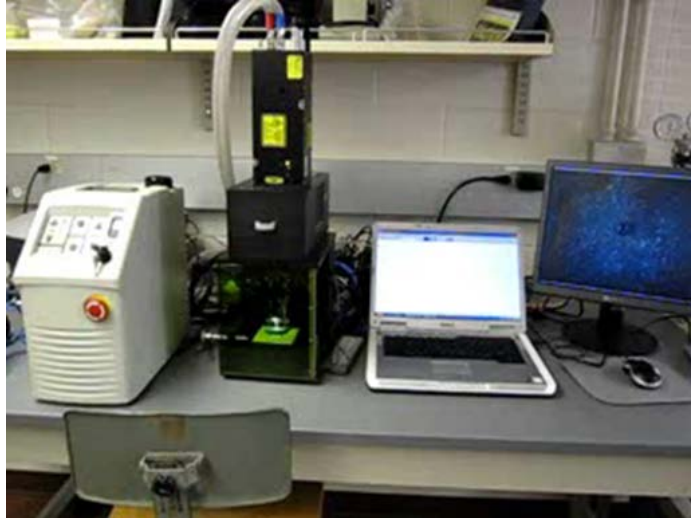


Figure 10 LIBS lab system at New Mexico State University.

Sample Analysis

During laser testing, individual aggregate particles were placed on a sample target platform in the sample chamber (the black housing under the laser shown in Figure 10) for LIBS analysis. The laser was focused on the surface; one shot was collected from each particle. The laser power was 120 mJ.

The TXDOT quartz sample used in the chert-quartz calibration and the APAC-Central samples consisted of sand-sized particles. Because the manipulation of individual sand grains in the sample chamber was found to be cumbersome, the sand from TXDOT and APAC Central were placed in a shallow aluminum dish with vertical sides, and the dish was placed on the target platform. The top surface of the sand was level with the top of the dish. The laser was set to shoot at 1Hz, and the sample was moved horizontally below the laser between shots. While this process results in some poor spectra due to poor focus and simultaneous analysis of two adjacent grains, the data can be reliably modeled (see TXDOT section below). This suggests that moving to an automated sampling and analysis system is highly feasible (see Plans for Implementation).

Multivariate Statistical Modeling

A total of nine different models, listed in Table 2, were developed in this effort. The number of models developed, the model reference name, the dependent variable modeled, the predictor type and the number of spectra averaged to create a single-spectrum for input to the model are also listed in Table 2, and discussed in greater detail in each respective state section below.

Early in this project, models were built using single-shot data, (i.e., each laser shot was used as a single spectrum). However, the modeling results improved radically by averaging spectra prior to multivariate modeling. Averaging improves results for two main reasons. First, averaging reduces the effects of the shot-to-shot variability inherent to LIBS analysis. Because there is essentially no sample preparation, samples differ

from one another in subtle ways such as surface roughness and angle between the surface and the laser light. These variations cause the laser to couple with the sample surface in different ways, resulting in shots with variable overall intensity. Averaging a large number of shots smoothes out these differences. Furthermore, averaging a large number of spectra captures the full chemical variability in the sample. Geologic materials are notoriously heterogeneous; compositions can vary even in materials that appear homogeneous.

The column labeled “predictor type” in Table 2 lists for each respective model the type of evaluation procedure used to generate the model output. Models with compositional predictor types (Table 2) correlate the spectra with a compositional variable; for example the percent analyzed insoluble residue (AIR), the percent carbonate in a silicate-carbonate mixed aggregate, and the percent chert in a chert-sand mixture. For these models, all of the spectra collected from a sample (100 or 150) were averaged to make a single spectrum for the sample. The models were tested using separate validation samples not included in the model calibration.

Table 2. Model Development Summary Table

Agency	Model Reference	Dependent Variable	Predictor Type	Number of Spectra Averaged
NYSDOT	NYAIR	Acid Insoluble Residue Content	Compositional Calibration Curve	150
NYSDOT	NYNCC	Noncarbonate-Carbonate Blend Content	Compositional Calibration Curve	150
KSDOT	KSSBI	Quarry Bed Identification	Matching Algorithm Indicator Integer (Yes = 1; No = 0)	10
KSDOT	KSDPF	D-Cracking Pass/Fail Test	Indicator Integer (Yes = 1; No = 0)	10
TXDOT	TXRC	Reactivity of Chert	Indicator Integer (More reactive = 1; Less reactive = 0)	30
TXDOT	TXCSI	Chert Source Identification	Matching Algorithm Indicator Integer (Yes = 1; No = 0)	30
TXDOT	TXCQS	Chert-Quartz Sand Content	Compositional Calibration Curve	100
APAC	OKC	Chert Content in Sand	Compositional Calibration Curve	500
APAC	OKF	Fe Content in Sand	Compositional Calibration Curve	500

Models with indicator integer predictor types (Table 2) correlate the spectra with the integers "1" and "0," where these indicator integers display the dependent variable of interest. For example, "1" means pass and "0" means fail in the KSDPF D-cracking pass/fail test. For these models, half of the spectra were used to create the model, and the other half were used in test-set validation. The acquired spectra were averaged in groups of 10 or 30 in an effort to minimize the shot-to-shot variability while still producing a statistically robust model. The matching algorithm models were a combination of a sequential stepwise procedure of comparing one bed to the next and an integer indicator model to provide a "match" or "no match" answer.

Averaged spectra were modeled using PCA (Principal Components Analysis) and PLS (Partial Least Squares Regression) techniques with the software Unscrambler (Camo Software, Inc.).

NEW YORK STATE: FRICTION AGGREGATES

Objectives and Analysis

NYSDOT Material Method (MM) 28 [8] covers the quality control procedures and criteria required to determine the acceptability of aggregate use in New York State hot mix asphalt and Portland cement concrete surface courses. The primary concern is the presence of an excessive carbonate component, which being softer than the silicate component, is susceptible to tire polishing and becomes slick when wet.

Three types of aggregate or aggregate blends are permitted by NYSDOT surface course specifications. They include:

1. Silicate rocks with little or no carbonate,
2. Carbonates with more than 20% acid insoluble residue (the silicate component),
and
3. Any mixture with a greater than 20% silicate aggregate.

A two-stage procedure is used by NYSDOT to qualify aggregate use in surface courses. If the aggregate is a carbonate, the AIR content must exceed 20%, by weight of aggregate, for the aggregate to be used. If the carbonate has less than 20% AIR, the carbonate must be blended with at least 20% of a silicate aggregate to be used. This evaluation process is illustrated in Figure 11.

Two calibration models were developed to predict the AIR content of carbonates, and the silicate content of a blended silicate rock-carbonate mix in accordance with the process illustrated in Figure 11. These two models are referred to as the New York Acid Insoluble Residue (NYAIR) model and the New York Noncarbonate-Carbonate Blend (NYNCC) model. NYSDOT submitted two sets of samples, listed respectively in Table 3 and Table 4, to support the development of the two models.

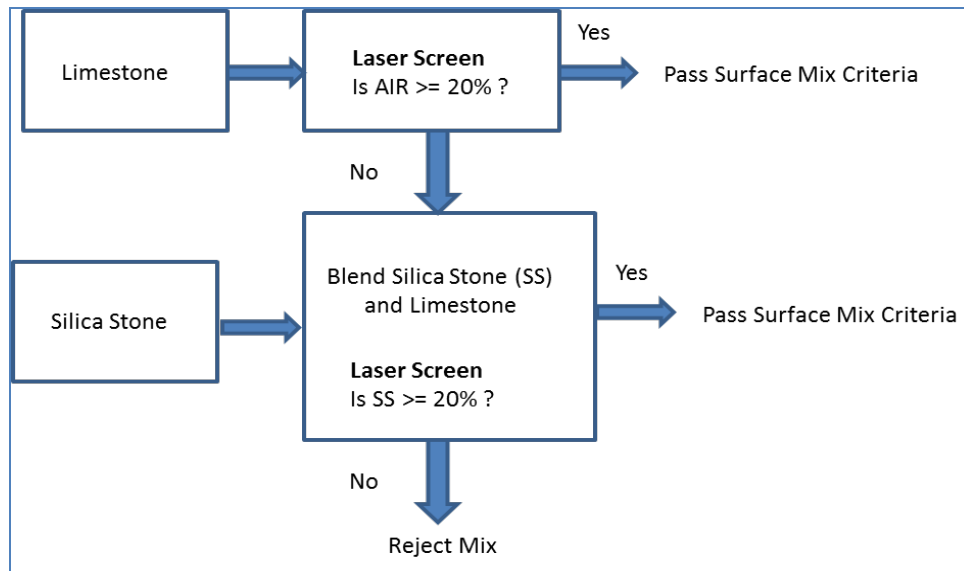


Figure 11 Friction aggregate quality control procedures in New York.

Table 3. Ten NYSDOT AIR Calibration Samples

Sample	% Residue
Limestone 8-17R	56.7
Limestone 2-9R	3.7
1-23R (10GP1024) limestone	31.5
2-6RS1 (10GP17S) dolostone and limestone	23.9
3-8RS (10GP998) dolostone	46.3
4-3RS (10GP1055) cherty limestone	38.6
4-10RS (10GP925) cherty limestone	37.5
4-12R (07GPC12) cherty limestone	33.1
5-3R (10GP1015) cherty limestone	38.4
8-15RS (10AR29S) limestone	36.7

Table 4. Additional Eight NYSDOT Carbonate-Noncarbonate Calibration Samples

Sample	Rock Type
2-16R	Granite
8-24R	Traprock
Sample 1 carbonate	Limestone, AIR unknown
Sample 1 silicate	Carbonate/Noncarbonate Blend
Sample 2 carbonate	Limestone, AIR unknown
Sample 2 silicate	Carbonate/Noncarbonate Blend
Sample 3 carbonate	Limestone, AIR unknown
Sample 3 silicate	Carbonate/Noncarbonate Blend

Modeling Procedures: NYAIR Model-Acid Insoluble Residue

Calibration of the NYAIR Model proceeded as follows:

1. Ten carbonate samples, listed in Table 3, with AIR contents ranging from 3.7 to 56.7% were available to develop a calibration for percent AIR.
2. Eight of the 10 carbonates with known AIR were used to construct the NYAIR calibration model; samples 8-15R and 4-10RS were withheld for test-set validation.
3. A total of 150 aggregate particles from each of the 8 samples was analyzed with one laser shot per particle,
4. The 150 spectra were averaged to produce one spectrum per sample.
5. The resulting spectra were regressed in the PLS NYAIR model against the known AIR content of each of the 8 samples in the calibration set.

Test-set validation proceeded as follows:

1. The test-set validation samples (8-15R and 4-10RS) consisted of two carbonates with known AIR content.
2. A total of 150 aggregate particles from each of the 2 carbonate samples were analyzed with one laser shot per particle,
3. The 150 spectra were averaged to produce one spectrum per sample.
4. The resulting spectra were input to the NYAIR calibration model to predict the AIR content of the test sample.

Modeling Results: NYAIR Model-Acid Insoluble Residue

The NYAIR calibration model developed to predict the AIR content of carbonate samples, shown in Figure 12, exhibited essentially perfect correlation. Two samples

were used for test-set validation (Table 5). The predicted AIR for these samples were within 1.2% of the true values. The test set validation was highly satisfactory.

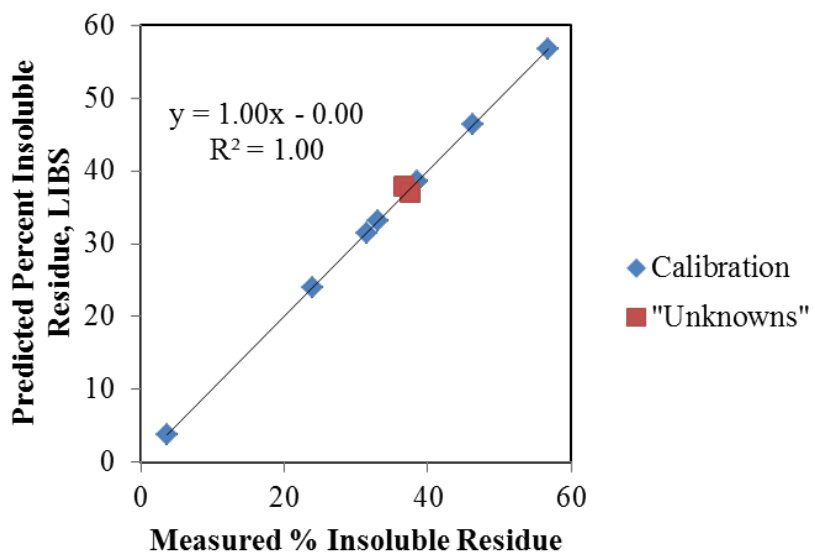


Figure 12 NYAIR calibration model for AIR content in NYSDOT carbonates.

Table 5. Determination of Percent AIR in Two Carbonates

Test-set Sample	Known AIR Value	Predicted AIR Value	Absolute Error
8-15R	36.7	37.9	1.2%
4-10RS	37.5	37.0	-0.5%

The NYAIR calibration model accuracy is attributed to the relative large data base (150 shots per sample) and the fact that the LIBS spectra seems to readily resolve differences between the carbonate and noncarbonate fractions of an aggregate particle.

Modeling Procedures: NYNCC Model - Percent Noncarbonate in Carbonate-Noncarbonate Blend

A total of 18 samples were available to calibrate and test the noncarbonate-carbonate aggregate model (Tables 3 and 4). All spectra generated were based on laser shots on 150 separate particles and the 150 spectra were averaged to yield one spectrum per sample.

Test-set validation was also used to test the NYNCC Model. The test-set validation samples consisted of three mixed blends of carbonate and silicate rock discussed below.

Calibration of the NYNCC Model proceeded as follows:

1. Sample 2-16R (a single noncarbonate aggregate, granite), and Sample 2-9R (a low-residue limestone) were selected for use in model calibration (See Table 3 and Table 4).
2. A total of 150 aggregate particles from each of the samples were analyzed with one laser shot per particle,
3. The 150 spectra were averaged to produce one spectrum per sample.
4. Weighted spectra were then developed to reflect anticipated spectra for samples containing 10% carbonate rock and 90% silicate rock, 20% carbonate rock and 80% silicate rock, etc., up to 90% carbonate rock and 10% silicate rock.
5. The resulting spectra were regressed in the PLS NYNCC model against the actual percent noncarbonate rock content, expressed as the percent of particles.

Test-set validation of the NYNCC Model proceeded as follows:

1. Sample 8-24R (a silicate aggregate, traprock), and Sample 4-12R (a high residue limestone, with a 33.1% AIR content) were selected as the validation samples (See Table 3 and Table 4).
2. Again, a total of 150 aggregate particles from each sample were analyzed with one laser shot per particle.
3. The 150 spectra were averaged to produce one spectrum per sample.
4. Weighted spectra were then developed, similar to the calibration set to reflect anticipated spectra for samples containing 33%, 50%, and 67% noncarbonate rock.
5. The resulting spectra were input to the NYNCC calibration model to predict the percent carbonate stone in the test sample.

Modeling Results: NYNCC Model - Percent Noncarbonate in Carbonate-Noncarbonate Blend

The NYNCC model is presented in Figure 13. This calibration was also excellent, suggesting again that carbonate and silicate resolution is very high and, if sufficient amounts of data are collected, the model can be very precise.

Test-set validation was also effective. Despite the differences between the calibration samples and the test-set samples, the model was able to effectively predict the percent silicate rock in the mixtures, as shown in Table 6. In this case, the absolute errors varied from 4.2 to 9.3%. These results would improve if additional mixtures of noncarbonate rocks (e.g., granite, traprock, sandstone, etc.) and a variety of carbonates with different AIR values were available to increase the robustness of the model.

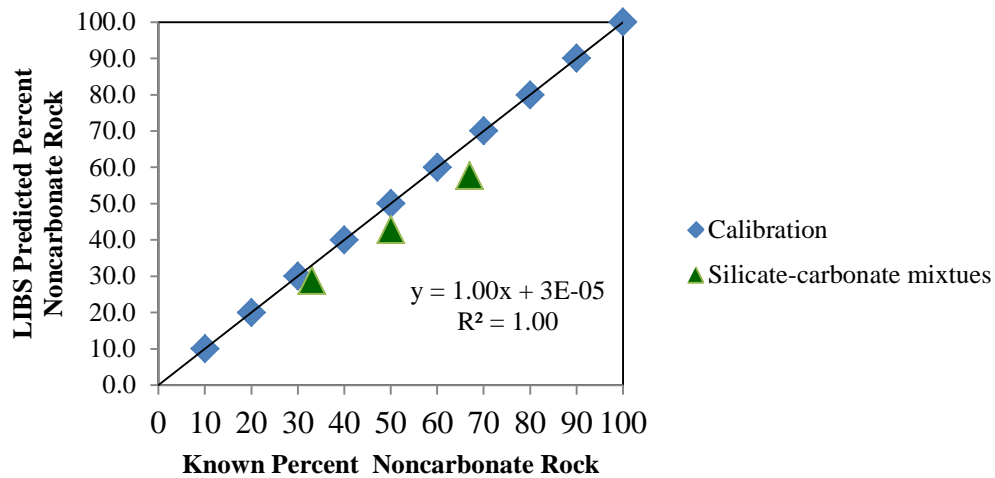


Figure 13 Calibration curve for percent noncarbonate rock in a noncarbonate-carbonate aggregate blend.

Table 6. Determination of Silicate Rock Content in Three Mixtures of Traprock and a Moderate-Residue Limestone

Test-Set Sample	Known % Noncarbonate Rock	Predicted % Noncarbonate Rock	Absolute Error
33% 4-12R + 67% 8-24R traprock	67	57.7	9.3 %
50% 4-12R + 50% 8-24R traprock	50	42.8	7.2 %
67% 4-12R + 33% 8-24R traprock	33	28.8	4.2 %

STATE OF KANSAS: D-CRACKING AGGREGATES

Objectives and Analysis

D-cracking of a Portland cement concrete pavement, a particular problem in Kansas and many Midwestern States is generally attributed to the destruction of the aggregate by cycles of freezing and thawing. Despite extensive study, the specific aggregate-related property that induces a D-cracking pavement is not known. KSDOT requires that aggregates incorporated into Portland cement concrete pavements (a Class 2 KSDOT

aggregate) be directly subjected to modified freeze thaw (soundness) testing. In addition, concrete specimens made with the subject aggregates must be resistant to rapidly repeated cycles of freezing and thawing in the laboratory. These test methods are defined by two KSDOT test methods [9]:

1. Modified freeze-thaw test (KTMR-21); must score 85 or better to be a usable aggregate.
2. Expansion test (KTMR-22); % expansion cannot exceed 0.025%; and Durability factor test (KTMR-22); score must be 95 or greater.

Samples that do not pass the first test are rejected and do not undergo the second test.

The objectives in the KSDOT effort were twofold: 1) to identify the source quarry bed from unknown samples and 2) to anticipate overall pass/fail D-cracking test results. As a result, two general models were developed.

The first model, referred to as the Kansas Source Bed Identification (KSSBI) model, was designed to determine from which bed an unknown aggregate was derived, and in the process identify quarry beds that were pre-certified as either high quality (e.g., Class 1 or 2) or lower-quality aggregate. The second model, referred to as the Kansas D-Cracking Pass/Fail (KSDPF) model, was designed to predict whether an aggregate would pass or fail KTMR-21 and KTMR-22 test methods.

KSDOT supplied 16 aggregate samples for testing from three quarries, listed in Table 7. Each of the 16 samples was derived from a separate bed within its respective quarry. The 16 samples, all limestone, included samples that failed KTMR-21, samples that passed KTMR-21, but failed KTMR-22, and samples that passed both KTMR-21 and KTMR-22. Samples were provided by KSDOT from four formations (geologic units), with samples from the same formations from different quarries to test spatial variability in the units.

As part of the calibration and validation process, for both the KSSBI and KSDPF models, each of the 16 separate samples was processed as follows:

1. For each bed (or sample) 100 separate aggregate particles were collected and divided into 10 separate subsamples, each containing 10 aggregate particles.
2. Each of the 10 particles within a subsample was analyzed with one laser shot; this resulted in 10 laser shots and 10 corresponding spectra per subsample.
3. The 10 spectra were averaged to yield one average spectrum per subsample.
4. Half, five of the 10 subsamples were randomly selected, as a training or calibration set, and the remaining five were reserved for test-set validation.

Table 7. KSDOT Calibration and Validation Samples

Formation	Member and Bed	Pass or Fail
<i>Quarry 1-046-16, Johnson County, 38.8377°N, 94.8693°W</i>		
Stanton Limestone	Stoner A	Fail KTMR-22
Stanton Limestone	Stoner B	Fail KTMR-22
<i>Quarry 4-030-02, Franklin County, 38.65413°N, 95.25246°W</i>		
Stanton Limestone	South Bend 1	Fail KTMR-22
Stanton Limestone	Stoner 2	Fail KTMR-22
Stanton Limestone	Stoner 3	Fail KTMR-22
Stanton Limestone	Stoner 4	Pass
Stanton Limestone	Stoner 5	Pass
Stanton Limestone	Stoner 6	Fail KTMR-21
Plattsburg Limestone	Spring Hill (SPGH) 12	Fail KTMR-21
Plattsburg Limestone	Spring Hill (SPGH) 13	Pass
Plattsburg Limestone	Spring Hill (SPGH) 14	Pass
<i>Quarry 4-002-01, Anderson County, 38.34605°N, 95.25555°W</i>		
Stanton Limestone	Captain Creek 2	Pass
Plattsburg Limestone	Spring Hill (SPGH) 3	Pass
Plattsburg Limestone	Spring Hill (SPGH) 4	Pass
Plattsburg Limestone	Spring Hill (SPGH) 5	Pass
Plattsburg Limestone	Spring Hill (SPGH) 6	Pass

Modeling Procedures: KSSBI Model-Source Bed Identification

The Kansas Source Bed Identification (KSSBI) model development issue revolved around how to calibrate and validate a model in such a manner that an unknown sample (spectra) could be introduced and matched to one of the 16 beds effectively. When focusing on 16 separate beds (all limestone) it became apparent during initial analyses that a simple comparison of all 16 spectra would not satisfactorily resolve differences between the individual beds. It was determined that a model was needed that was of sufficient resolution to identify more subtle differences in spectra.

After several starts and stops, the calibration approach selected involved the use of a matching algorithmic process, based on work by R. Multari and others at Applied Research Associates, Albuquerque, NM (patent pending) [10]. In this procedure, the spectra derived from the samples are compared to one another in a stepwise manner by comparing the relationship of an “unknown sample spectra” to the spectra derived from “all the other beds.” This methodology provided the means to effectively identify the specific identity (e.g., bed) of an unknown sample.

One way to think of the procedure is as follows: If one has 16 beds, labeled A, B, C, D, E.....P, then the spectra of Bed A will relate to all other spectra in a unique and distinct manner, the spectra of Bed B will relate to all the other spectra in a different unique and definable manner and so on. While this is a somewhat simplified view of the

analysis it is sufficient to provide a conceptualization of the procedure, which is described in detail below.

Calibration of the KSSBI matching algorithm model involved the development of 15 separate models. Each of these models were designed to identify one of the 15 beds. The 16th bed would be unrecognized by the first 15 models. The developmental process involved the selection of an

- Optimum sequence for examining an unknown sample (Sample X) with each of the 15 models generated (e.g., Model 1, Model 2....Model 15), as well as the
- Criteria by which the unknown sample (Sample X) could be correlated with one of the 16 beds in each of the 15 models.

The specific steps taken to develop the KSSBI model and a brief summary of those steps will hopefully provide some clarification:

1. Generate a Principal Component Analysis (PCA) score plot using all calibration samples (i.e., the average spectrum of the five subsamples used as the calibration set in each of the 16 beds)

A PCA score plot, as previously outlined, is a projection of the original data onto a new coordinate axis system (Principal Components). The PCA score plot projection groups samples with similar characteristics together in the new coordinate system and provides a means to see if the sample types used can be differentiated. Figure 14 shows the PCA score plot for the 16 limestone beds.

3. Select Model 1 of the 15 model sequence

The first step in the analysis was to identify one bed in the PCA score plot that was distinct from all others. This bed was Spring Hill 14. Springhill 14 plots in a different space than all the other beds (Figure 14). Filled circles are for sample Springhill 14, which is compositionally distinct from all the other samples (open triangles). This distinctness of Springhill 14 suggests that Springhill 14 will be one of the easiest beds to identify. Thus, it is determined that Model 1 in the overall 15 model program would compare Springhill 14 to all other beds.

4. Determine the criteria to be used to correlate an unknown sample with Springhill 14 in Model 1

A Partial Least Squares (PLS) Regression model was produced to discriminate between Springhill 14 and all the other beds. The PLS model created was an Integer Indicator model in which the selected bed (in this case, Springhill 14) was assigned the indicator value "1" and all other beds were assigned the value "0." When an Integer Indicator PLS model is used in such a manner, the PLS model regresses each spectra relative to the set indicator values and provides a score in the "approximate" range of 0 to 1 for all input spectra. This regression is shown in Figure 15. Spring Hill 14 spectra have predicted values greater than 0.5, i.e., closer to "1," and all other samples have predicted values less than 0.5, i.e., closer to "0." The Value of Apparent Distinction (VAD) was selected at 0.5. This was accepted as a useful model because it discriminates between the two groups.

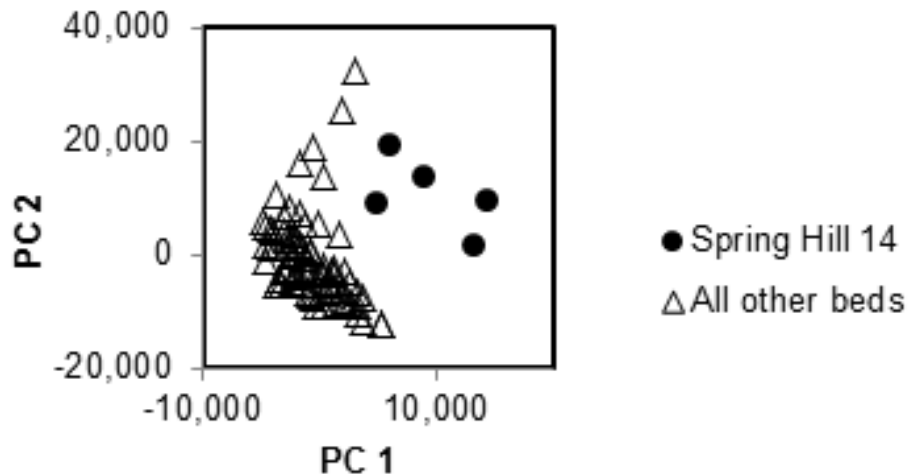


Figure 14 PCA score plot for the 16 limestone beds used in the KSSBI Model.

5. Select Model 2 of the 15 model sequence
Spring Hill 14 was then removed from the data set and a new PCA score plot was made for the remaining beds. This score plot identified Stoner 4 as most distinct from the remaining beds and so Stoner 4 was selected as Model 2.

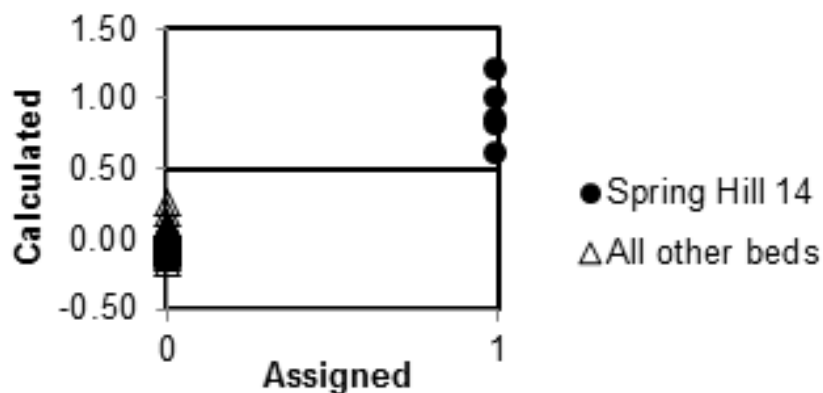


Figure 15 Model 1 PLS indicator integer regression in the KSSBI.

6. Determine the criteria to be used to correlate an unknown sample with Springhill 14
A PLS model was created in which the selected bed (in this case, Stoner 4) is assigned the indicator value "1" and all other beds are assigned the value "0." Model 2 was accepted because it was found to discriminate between the two groups.
7. Develop remaining sequences of models

The process was repeated until all beds were identified. The resulting matching algorithm is depicted in Figure 16.

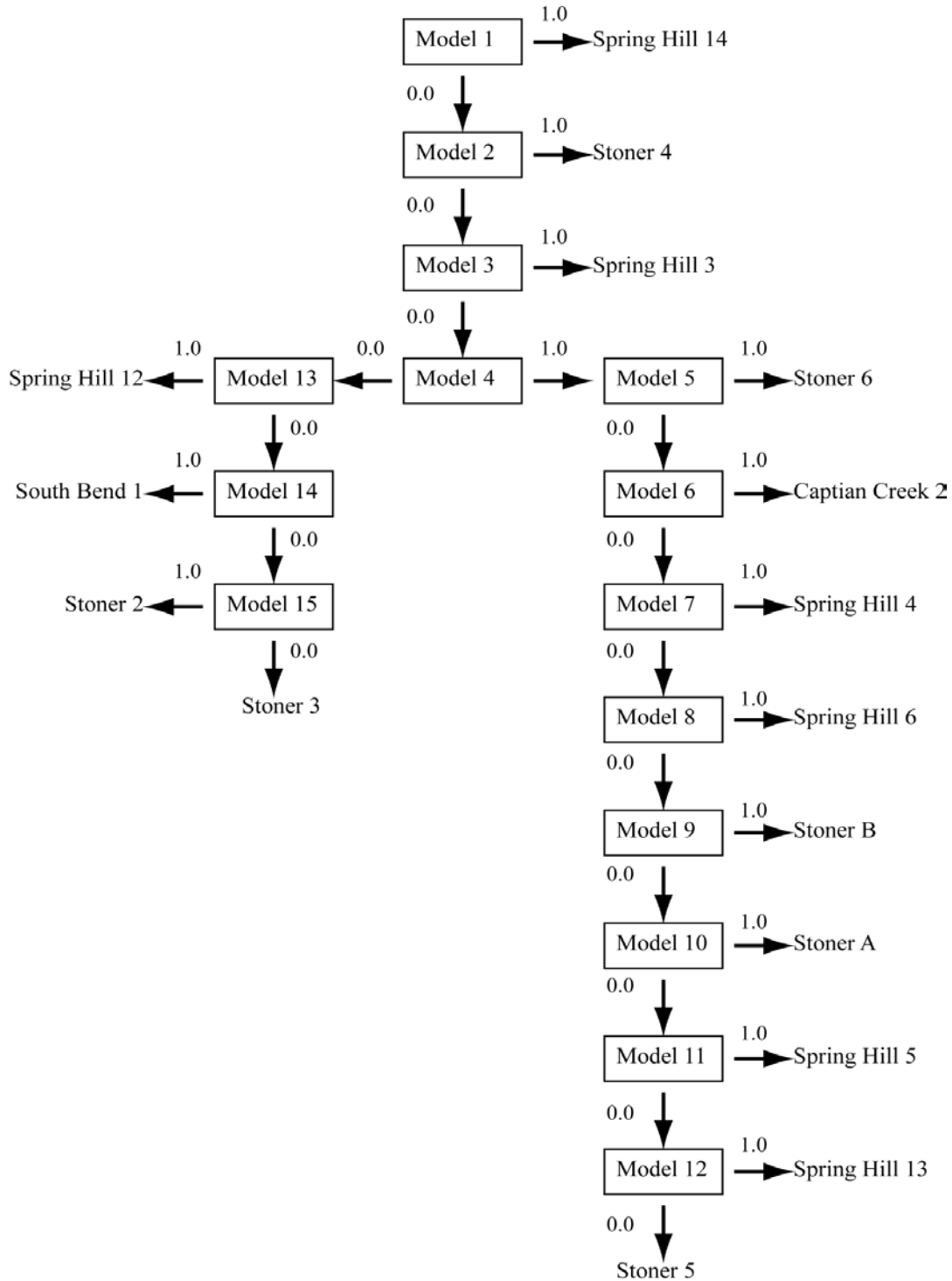


Figure 16 KSSBI matching algorithm for identification of aggregate source beds.

8. Branch Model 4 in the matching algorithm.

The algorithm was intentionally split into two branches at Model 4 with two separate arms. This was done because a single bed was not uniquely distinguishable in the PCA scoring plot for Model 4. The remaining beds at this point were found to cluster into two well-defined groups. This is illustrated in Figure 17, where the two groups are identified as filled circles and open triangles. Model 4 was split into Model 5 and Model 13, each containing one of the distinguishable groups. After splitting the model, the remaining beds were identifiable and the modeling sequence was completed.

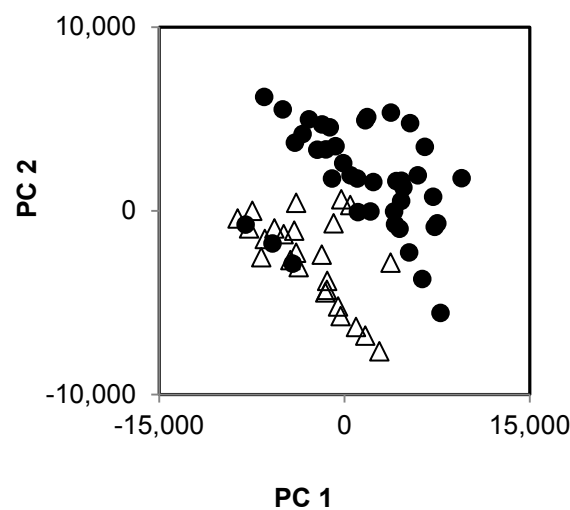


Figure 17 PCA score plot for Model 4 of KSSBI, in which the beds are separated into two groups.

In summary, the calibrated KSSBI model compares each bed in turn to the other beds, removing a bed once it has been identified. By comparing only one bed to all the other beds, the unique characteristics of the bed are better recognized by the model. Also, because beds are sequentially removed from the model, the model is able to recognize the small differences between beds late in the model. When all beds are compared simultaneously, these small differences are insignificant and thus the beds are indistinguishable.

The order of selection of each bed in the algorithm, as shown above, is not random. It is based on an analysis of PCA models (score plots) to identify beds that are readily identifiable (do not readily blend in with the other spectral data). Those beds that are most distinct are modeled first in the hierarchy. The bed spectra become more similar to each other as one proceeds through the modeling hierarchy by design.

Modeling Results: KSSBI Model-Source Bed Identification

Validation of the KSSBI matching algorithm model proceeded as follows:

1. The five reserved spectra for each bed were used for test-set validation of the models in the matching algorithm.
2. All reserved spectra were run through each of the 15 models and predicted integer values were determined for each unknown sample.
3. An unknown sample (Sample X) was identified when it matched with the appropriate VAD (generally greater than 0.5).

An example of this validation procedure is shown in Figure 18 for Model 1. Note that the predicted values in Figure 15 were calculated for the spectra used in the calibration. The predicted values in Figure 18 were calculated for the reserved (test-validation) spectra that were not used in the calibration.

Table 8 lists the success rates for the matching algorithm, calculated as the number of correctly identified beds. The source bed for all the individual subsamples used in the validation set were correctly predicted over 90% of the time for all subsamples with the exception of Models 12 (80%), and 15 (60%), which are at the bottom of the matching algorithm (see Figure 16). The beds in these models are chemically very similar, and thus more difficult to distinguish from each other. Overall, however, these success rates were found to be excellent given the minimal number of samples used in calibrating the model.

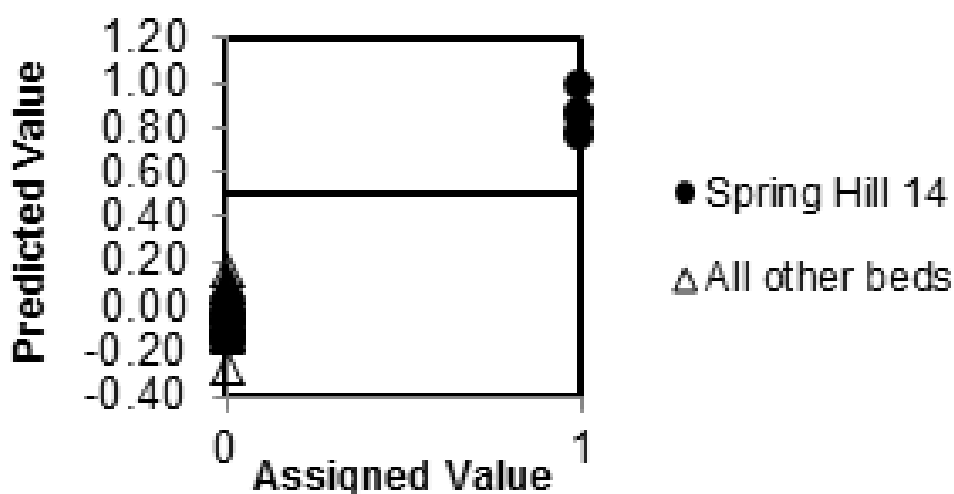


Figure 18 Results of Model 1 test-set validation.

Table 8. Success Rates for KSSBI Algorithm

Model Number	Success, averaged spectra	Success, averaged beds
1	100 %	100 %
2	100 %	100 %
3	100 %	100 %
4	96 %	100%
5	100 %	100 %
6	98 %	100%
7	100 %	100 %
8	100 %	100 %
9	100 %	100 %
10	100 %	100 %
11	100 %	100 %
12	80 %	100 %
13	100 %	100 %
14	93 %	100 %
15	60 %	100 %

It is noteworthy, that success rates can be increased to 100% by averaging the spectra from each of the five test validation subsamples. One average indicator value eliminates the particle to particle variability that could arise in a small sample set such as the one used in calibrating and validating the model. As an example, Figure 19 shows how averaging the subsamples can transform an 80% successful model (Model 12) to a 100% successful model. The model is considered 80% successful because of the 10 subsamples used two did not predict correctly. These two were Spring Hill 13 subsamples. Averaging the five predicted values for Spring Hill 13 results in an indicator value of 0.59 (greater than the VAD value of 0.5). Using the average predicted value of 0.59 this model would be considered 100% successful. In a real scenario, where a much larger number of particles and spectra would be averaged, this would almost certainly be the case. This concept is similar to analyzing a bucket of gravel. Although not every piece of gravel in the bucket may be correctly identified, the entire contents of the bucket can be correctly identified by averaging the results for the entire bucket.

Modeling Procedures: KSDPF Model – D-Cracking Pass/Fail Classification

The KSDPF model was developed to predict whether an aggregate would pass or fail the KTMR-21 or KTMR-22 test method. In the calibration, spectra were regressed against indicator integers with values of "1" for test passing samples and "0" for test failing samples. The reserved spectra were then fed into the model and success rates calculated from how many spectra were correctly identified as near 1 or near 0 (above or below the VAD).

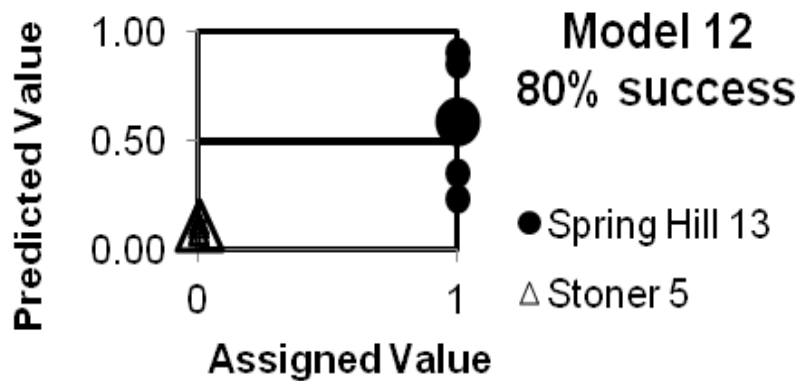


Figure 19 Model 12 subsample averaging (large circle and large triangle depict averages of subsamples resulting in 100% predictability).

Modeling Results: KSDPF Model – D-Cracking Pass/Fail Classification

As shown in Figure 20, the KSDPF model correctly predicts whether a sample will pass or fail the KTSM tests, at 100% success rate. The calibration model (top panel) results in 100% correct identification of the validation-set spectra (lower panel). Again, the success rate achieved by this modeling was judged to be quite remarkable, given the complexity of the D-cracking phenomenon. It would seem that D-cracking susceptible aggregates display a unique spectral fingerprint captured in the LIBS spectra and that multivariate modeling techniques are capable of resolving and classifying these spectra into pass and fail categories.

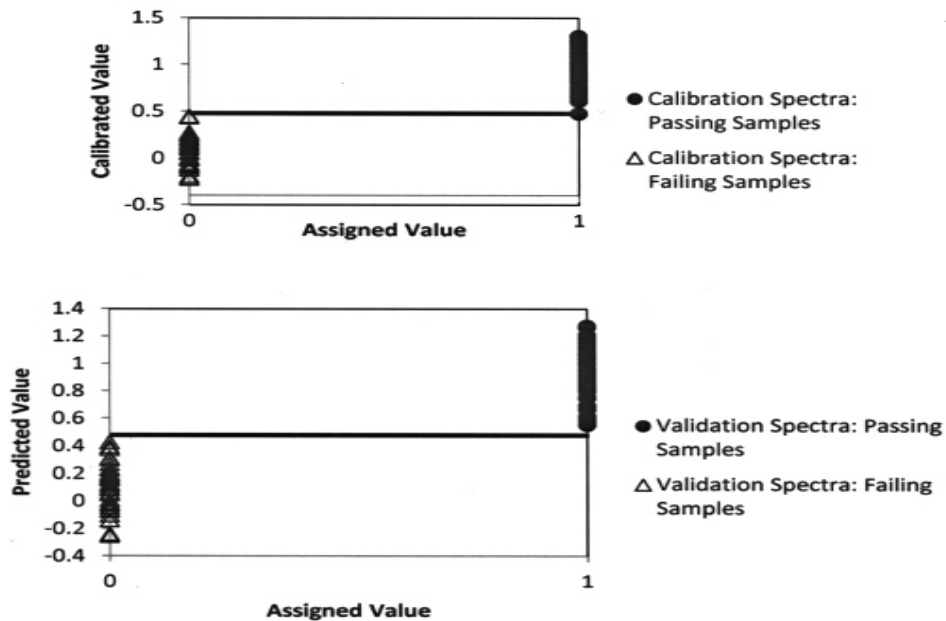


Figure 20 Calibration and validation results for KSDPF model. The calibration model (top panel) results in 100% correct identification of the test-set spectra (lower panel).

STATE OF TEXAS: ALKALI SILICA REACTIVE AGGREGATES

Objectives and Analysis

The primary focus of the Texas study was the identification of alkali silica reactive (ASR) aggregates. Alkali silica reactivity (ASR) in Portland cement results in potentially harmful expansion within the concrete structure. This expansion is commonly attributed to the formation of an unstable gel during reaction of reactive silica in the aggregate with alkali hydroxides in the Portland cement. The research effort focused on the identification of reactive cherts containing a microcrystalline form of silica that is commonly thought to be one of the sources of reactive silica.

More specifically, the TXDOT effort was designed to determine whether the laser-analysis could: 1) quantify the percent reactive chert in a chert-quartz blend, 2) classify a chert sample as either a high or low reactive sample and 3) differentiate and identify a particular chert sample from a pool of samples. As a result, three models were developed. The first model, a compositional model, referred to as the Texas Chert Quartz Sand (TXCQS) model, was designed to quantify the percent chert in a chert-quartz sand blend. The second model, referred to as the Texas Reactive Chert (TXRC) model was designed to classify cherts into one of two classes (high or low reactivity). The third model, the Texas Chert Source Identification (TXCSI) model, was designed to identify the source of an unknown chert sample.

Two TXDOT sample sets were used for testing:

1. The first sample set, used to develop the TXCQS model consisted of a reactive chert from the Adameek Pit and a non-reactive Ottawa quartz sand.
2. The second sample set, consisting of four reactive cherts (Hanson Servtex Dark, M&M Beckman, TX1 Tin Top, and Hanson Servtex Light); these were used to develop the TXRC and TXCSI models.

Modeling Procedures: TXCQS Model – Chert Content in Quartz Sand

The TXCQS model developed was compositional and designed to determine the percent chert in a chert-quartz mixture. The calibration proceeded as follows:

1. 100 laser shots were made on both the chert and quartz sand samples, resulting in 100 spectra for each sample.
2. The 100 spectra were averaged to yield one spectrum for both the chert and quartz, respectively.
3. Weighted spectra were then developed to reflect anticipated spectra for samples containing 10% chert and 90% quartz sand, 20% chert and 80% quartz sand, etc., up to 90% chert and 10% quartz sand.
4. The resulting spectra were regressed in the PLS TXCQS model against the percent chert value.

Test-set validation was performed by selecting a second set of chert and quartz sample. For this second set:

1. 100 laser shots were also made on both the chert and quartz sand samples, resulting in 100 spectra for each sample.
2. The 100 spectra were averaged to yield one spectrum for both the chert and quartz, respectively.
3. Weighted spectra were then developed, similar to the calibration set to reflect anticipated spectra for samples containing 10%, 20%, 30%, 50% and 60% chert.
4. The resulting spectra were input to the TXCQS calibration model to predict the percent chert content of the test sample.

Modeling Results: TXCQS Model – Chert Content in Quartz Sand

The TXCQS model calibration for the chert-quartz mixtures is shown in Figure 21. The test-set validation data, listed in Table 9, yielded very good results. The absolute errors ranged from 0.2 to 4.2%. Because LIBS can distinguish between chert and quartz, it is reasonable to suggest that the chert-quartz model will be strengthened by averaging together a variety of chert and quartz samples when constructing the model.

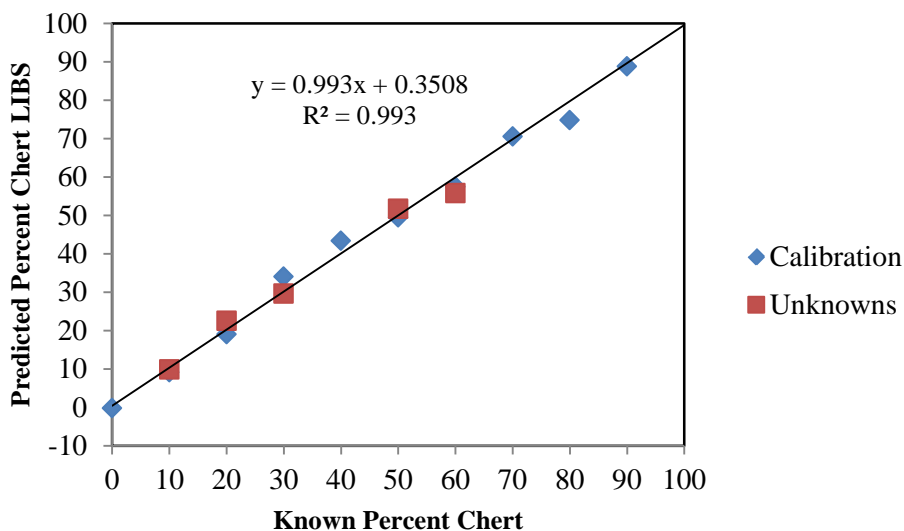


Figure 21 TXCQS calibration model for percent chert in a chert-quartz mixture.

Table 9. Results for Analyzed Mixtures of Chert and Quartz

Known % Chert	Predicted % Chert	Absolute Error
10	9.8	-0.2%
20	22.5	2.5%
30	29.6	-0.4%
50	51.7	1.7%
60	55.8	-4.2%

Modeling Procedures: TXRC Model – Reactivity Classification

The TXRC model was developed for the purpose of classifying unknown chart samples with respect to degree of ASR reactivity. In the calibration, spectra were regressed against indicator integers with values of "1" for the more reactive cherts and "0" for the less reactive samples. The reserved (validation sample) spectra were then fed into the model and success rates calculated from how many spectra were correctly identified as near 1 or near 0 (above or below the VAD).

TXDOT submitted four chert samples with known relative ASR reactivity for analysis. These are listed in Table 10.

Table 10. TXDOT Chert Samples Used in TXRC Model

Sample	Reactivity
Hanson Servtex Dark chert	Less
M & M Beckman	Less
TX1 Tin Top	More
Hanson Servtex Light chert	More

Reactivity was divided into two categories, based on TXDOT input: less reactive and more reactive. The calibration procedures were as follows:

1. For each chert sample, 150 spectra were acquired (one laser shot per 150 aggregate particles).
2. The 150 spectra were separated into 5 subsamples per sample, and the 30 spectra associated with each subsample were averaged to yield one spectrum per subsample.
3. Three averaged spectra (or 3 subsamples) were used to calibrate the model.
4. Two averaged spectra (or 2 subsamples) were used to validate the model.

The results of the integer indicator calibration process used to calibrate the TXRC model are graphically presented in Figure 22. A total of 12 spectra were used in the calibration, 6 with lower reactivity and 6 with higher reactivity. The regressed indicator values of the six spectra with lower reactivity are shown on the left side of the figure. The regressed indicator values of the six spectra with the higher reactivity are shown on the right side of the figure. The large circle and large triangle represent the average value of the indicator values for all the higher and lower reactivity samples, respectively. Instead of using a value of apparent distinction (VAD) value of 0.5 as in most other models, a value of 0.4 was used because it produced the best results in the calibration.

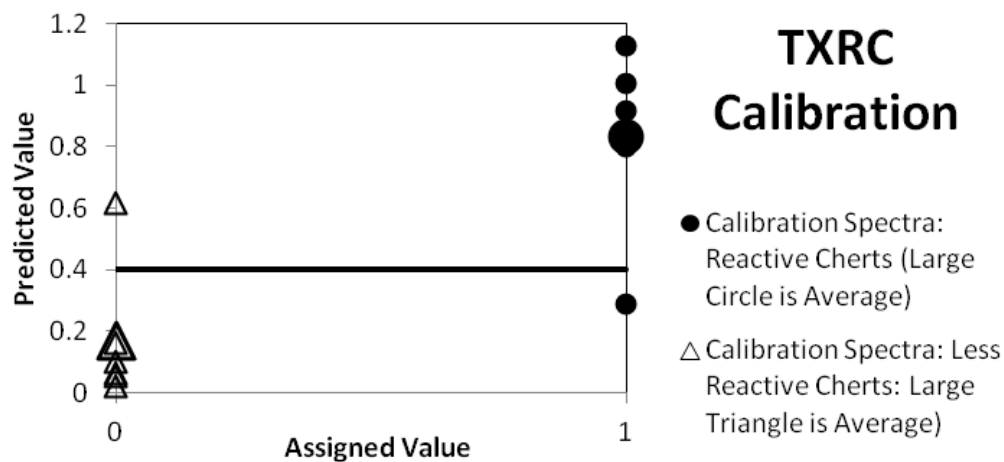


Figure 22 Calibration of TXRC model for classifying reactive and less-reactive chert types.

Modeling Results: TXRC Model – Reactivity Classification

The validation procedure was conducted with the two validation spectra. These were introduced into the model, and predicted integer values were calculated for each (unknown) test spectra. These results are shown in Figure 23. One spectrum was classified incorrectly in this model. There were 8 spectra used in validation; this is an 87% success rate.

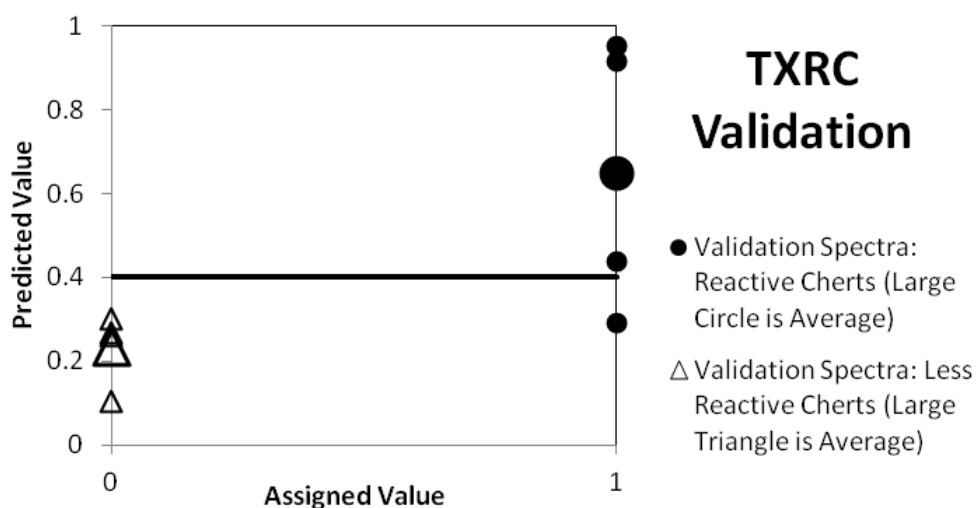


Figure 23 Validation of TXRC model for classifying reactive and less-reactive chert types.

It is noteworthy that if the average of all the subsamples were included in the model, then the success rate would be 100%. This can be seen in Figure 23, where the large circle and large triangle represent the average spectra values for the more and less reactive chert samples, respectively. The average of a greater number of subsamples is always above or below the VAD in accordance with the expected calibration.

Although this is a small pilot study, the technique shows enormous promise for the capability of rapid and accurate detection of reactive cherts. A larger study of > 20 chert samples of known reactivity would be useful to more fully determine the efficiency of the technique.

Modeling Procedures: TXCSI Model - Chert Source Identification

A matching algorithm model, the TXCSI model, was developed to identify a specific chert sample from the series of four chert samples available for testing. The four TXDOT cherts, listed in Table 10, were used to create the model, which was similar to the KSSBI model described previously. More detailed information on the matching algorithm model was presented in the introduction to the modeling procedures for the KSSBI model (page 20).

Calibration of the TXCSI matching algorithm model involved the development of three models. Each of these models was designed to identify one of the 3 cherts. The 4th chert would be unrecognized by the first 3 models.

As in the KSSBI model, the developmental process for the TXCSI model involved the selection of an

- Optimum sequence for examining an unknown sample (Sample X) with each of the 3 models generated (e.g., Model 1, Model 2 and Model 3), as well as the
- Criteria by which the unknown sample (Sample X) could be correlated with one of the 4 chert samples in each of the 3 models.

The specific steps taken to develop the TXCSI model and a brief summary of those steps were as follows:

1. Generate a Principal Component Analysis (PCA) score plot using all calibration samples (i.e., the average spectra of the five subsamples used as the calibration set for each of the 4 cherts)

A PCA score plot, as previously outlined, is a projection of the original data onto a new coordinate axis system (Principal Components). The score plot projection groups samples with similar characteristics together in the new coordinate system and provides a means to see if the sample types used can be differentiated. Figure 20 shows the PCA score plot for the 4 chert samples.

2. Select Model 1 of the 3 model sequence

The first step in the analysis was to identify the chert sample in the PCA score plot that was distinct from all others. This sample was TX1 Tin Top. TX1 Tin Top plots in a different space than all the samples (Figure 24). Filled circles are for sample TX1 Tin Top, which is compositionally distinct from all the other samples (open triangles). This distinctness of TX1 Tin Top suggests that this chert will be one the easiest beds to identify. Thus, it was determined that Model 1, in the overall 3 model program, would compare TX1 Tin Top to all other samples.

3. Determine the criteria to be used to correlate an unknown sample with TX1 Tin Top in Model 1

A Partial Least Squares (PLS) Regression model was produced to discriminate between TX1 Tin Top and all the other samples. The PLS model created was an Integer Indicator model in which the selected sample (in this case, TX1 Tin Top) is assigned the indicator value "1" and all other samples are assigned the value "0." When an Integer Indicator PLS model is used in such a manner, the PLS model regresses the spectra in relation to the set indicator values and provides a score in the "approximate" range of 0 to 1 for all input spectra. This regression is shown in Figure 25. The TX1 Tin Top spectra have predicted values greater than 0.5, i.e., closer to "1," and all other samples have predicted values less than 0.5, i.e., closer to "0." The Value of Apparent Distinction (VAD) was selected at 0.5. This was accepted as a useful model because it discriminates between the two groups.

4. Select Model 2 of the 3 model sequence

TX1 Tin Top was then removed from the data set and a new PCA score plot was made for the remaining samples. This score plot, shown in Figure 26, identified Hanson Servtex Light as most distinct from the remaining beds and so Hanson Servtex Light was selected as Model 2.

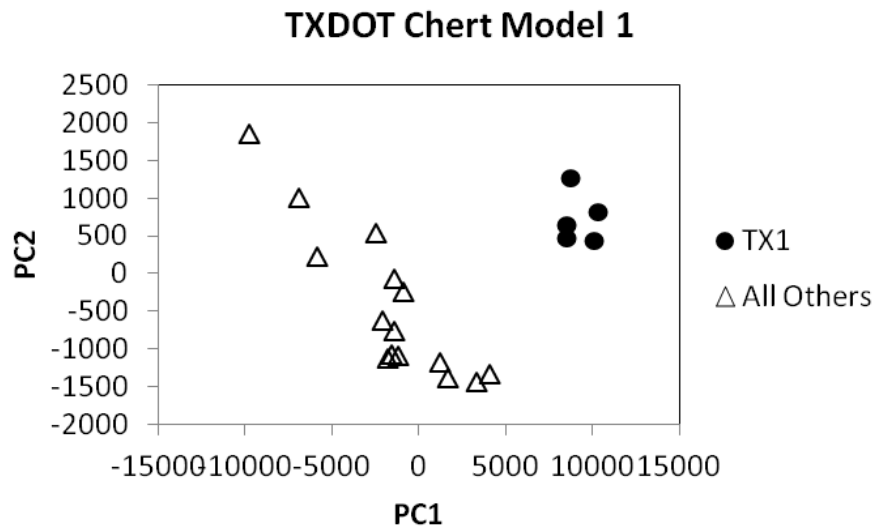


Figure 24 PCA score plot for the 4 chert samples used in the TXCSI model.

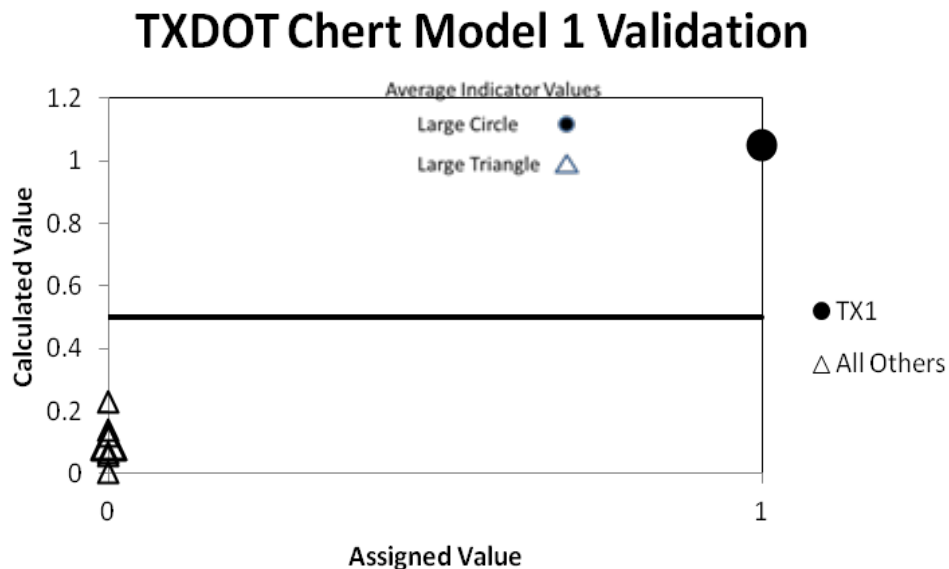


Figure 25 Model 1 PLS indicator integer regression in the TXCSI model.

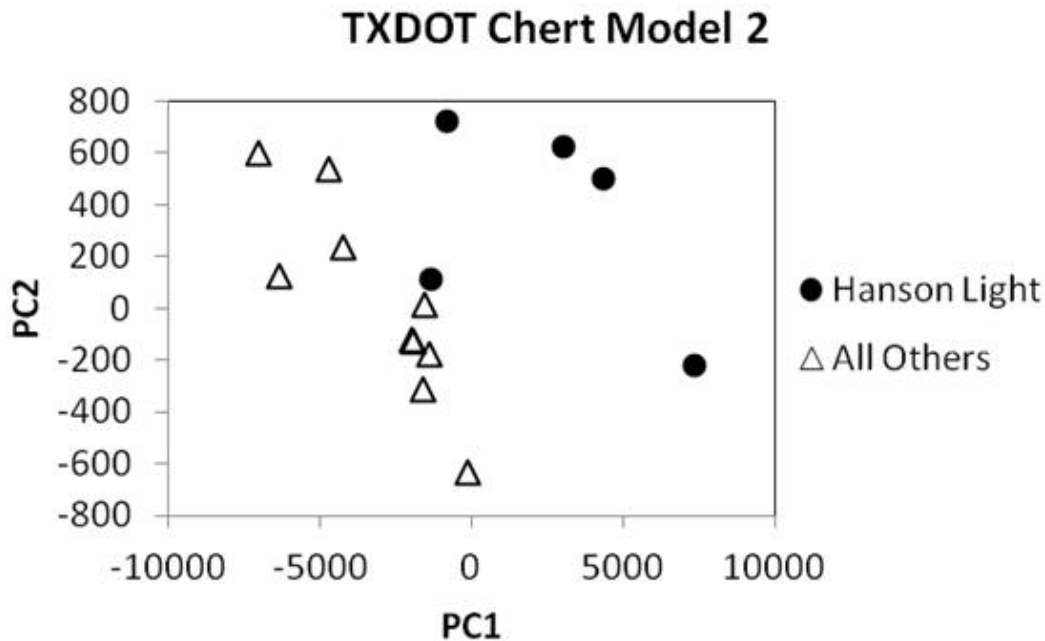


Figure 26 PCA score plot for the 3 remaining chert samples used in the TXCSI model.

5. Determine the criteria to be used to correlate an unknown sample with Hanson Servtex Light

A PLS model was created in which the selected sample (in this case, Hanson Servtex Light) was assigned the indicator value "1" and all other beds are assigned the value "0." Model 2, shown in Figure 27, was accepted because it was found to discriminate between the two groups.

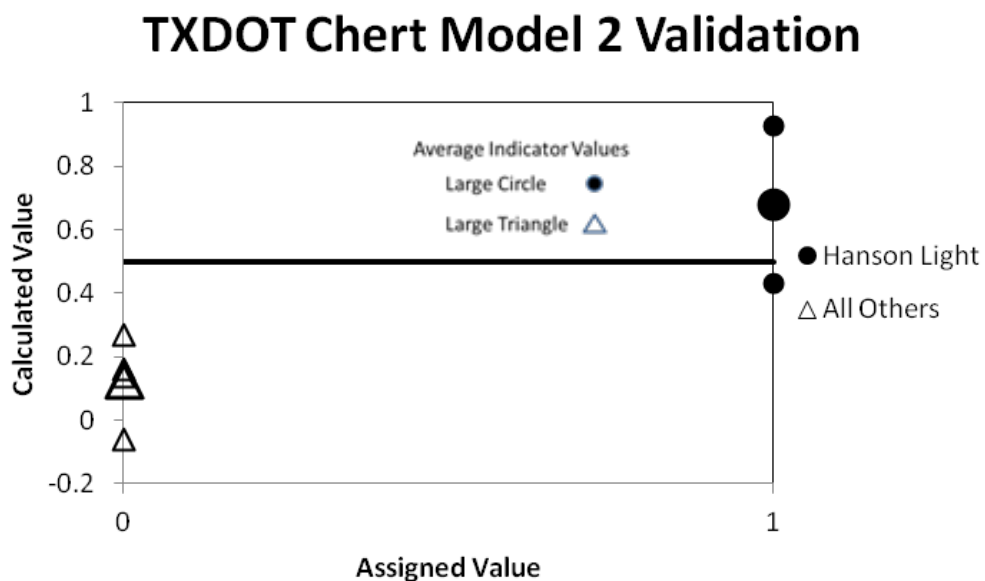


Figure 27 Model 2 PLS indicator integer regression in the TXCSI model.

6. Select Model 3 of the 3 model sequence

Hanson Servtex Light was then removed from the data set and a new PCA score plot was made for the remaining samples (Hanson Dark and M&M). This score plot, shown in Figure 28, shows the two remaining samples, which are readily distinguishable.

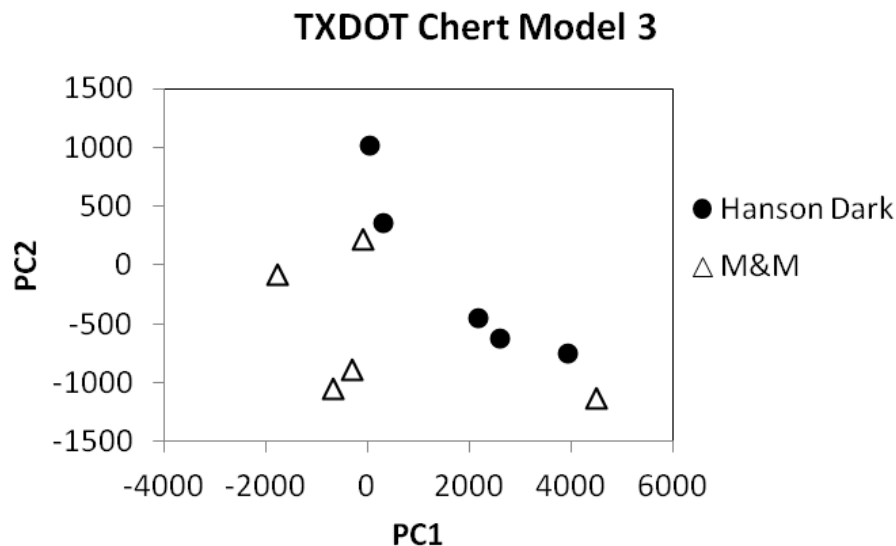


Figure 28 PCA score plot for the 2 remaining chert samples used in the TXCSI model.

7. Determine the criteria to be used to differentiate between the remaining two chert samples

A PLS model was created in which the two remaining chert samples were assigned indicator values of "1" and "0". Model 3 shown in Figure 29, was accepted because it was found to discriminate between the two groups.

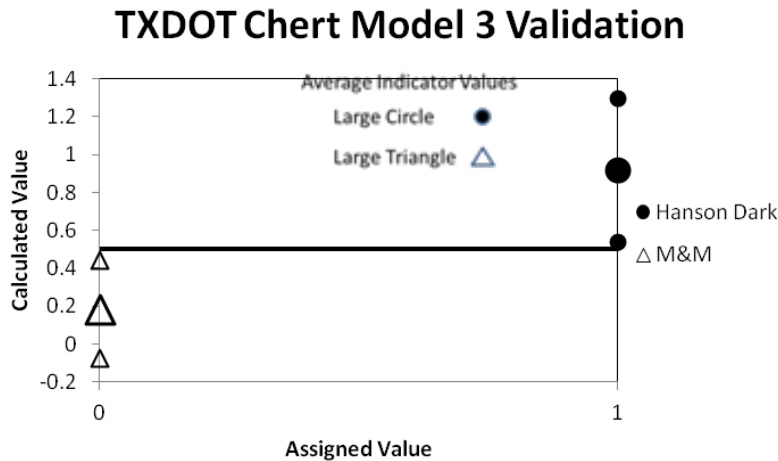


Figure 29 Model 3 PLS indicator integer regression in the TXCSI model.

Modeling Results: TXCSI - Chert Source Identification

The resulting matching algorithm is depicted in Figure 30. All three models were 100% successful when any of the validation set samples were introduced into the algorithm. Again, this is a small pilot study, and a larger study would be useful to further validate these findings. However, there is a high likelihood that LIBS analysis of ASR reactive chert samples will be effective in identifying specific cherts.

APAC-CENTRAL: ANALYSIS OF FINE AGGREGATES

Objectives and Analysis

The primary focus of the APAC-Central study was the quantitative analysis of certain components in fine aggregates. The analysis was different from the other studies because the small grain size of particles made it impractical to analyze each particle. Instead, spectra were taken as the laser moved across a layer of sand, simulating an automated process.

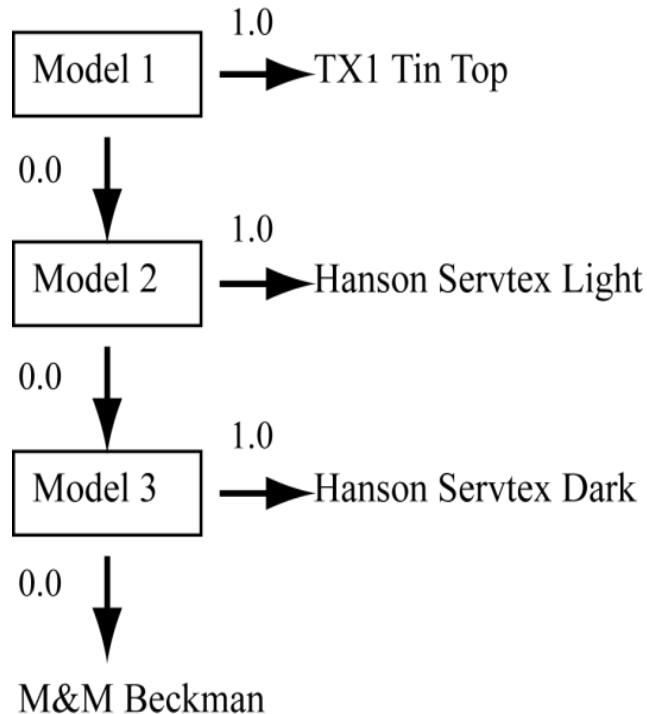


Figure 30 Matching algorithm model for TXDOT chert samples.

Two Arkansas River sands were analyzed for different components:

Van Buren Sand (chert content) The Van Buren sand is used as a general construction aggregate. The problem is ASR (alkali-silica reaction) when used as concrete sand. If the cement has a high alkali content and the sand has sufficient chert, ASR can be an issue. Traditionally, samples of Van Buren sand are occasionally sent to a mineralogist, who estimates chert content visually.

Muskogee Sand (Fe content) The Muskogee sand plant is about 200 miles up the Arkansas River from the Van Buren plant. The Muskogee plant produces general construction aggregate and some of the sand is sold to a glass plant. The sand is a reliable construction aggregate, containing mainly quartz and feldspar. For glass production, the Fe content must be reduced because Fe colors the glass. The glass sand undergoes two treatments before it is usable for glass production. Raw sand, with > 0.17 wt. % Fe passes through a bubble classifier that removes heavy particles; it is then passed through a high-intensity magnetic separator to remove magnetite (iron oxide). The resulting sand, called amber sand, typically has 0.14-0.17% Fe. To make glass sand, the amber sand is washed in HCl to remove iron oxide coatings. Glass sand typically has < 0.07 % Fe. Quality control is currently achieved by analyzing relatively small samples of sand by atomic absorption (AA).

Prior to analysis, approximately a quart of sand was split with a sample splitter to assure that no bias influenced each aliquot for analysis.

Van Buren Sand. For the Van Buren sand, several grams of sand were placed in an aluminum foil dish, and analyzed with the laser. The sample was moved under the laser as it fired at one shot per second. Focus was manually adjusted prior to each shot. Laser power was 180 mJ; the Q-switch delay was -1.5 μ s. One thousand (1,000) shots were acquired on each of two samples. The shots were averaged into two averages of 500, to provide two analyses of the same material. Two splits of Van Buren sand (VB-1 and VB-2) were analyzed in this way, yielding a total of four analyses.

The VB-1 and VB-2 splits were made into thin sections for visual inspection. The sands were impregnated with epoxy and sent to an external lab for thin section preparation. The mineral content of each split was determined by counting 500 points on each thin section.

Muskogee Sand. Three types of Muskogee sand were used in this project: raw (MR), amber (MA), and leached (ML). Three splits of each sand type were analyzed by LIBS, yielding nine analyses. One thousand shots were averaged by 500 in each analysis. In this case, the laser energy was 105 mJ and the Q-switch delay time was -1.5 μ s.

Because the calibration for the Muskogee sand was to be for weight percent Fe, two of the three splits for each sample were analyzed for Fe by atomic absorption at APAC-Central's Muskogee sand plant. The analyzed splits were MR-1, MR-2, MA-1, MA-2, ML-1, ML-2.

Modeling Procedures: APACC Model – Chert Content in Fine Sand

The TXCQS model developed with the Ottawa quartz sand and Adameek Pit Chert was used to analyze the percent chert in the Van Buren sand. It was not clear if this calibration would be appropriate for the Van Buren sand because the calibration included only quartz and chert, but the sand contains other minerals as well (Table 11). The LIBS measurements of percent chert were validated by comparison with point-count data.

Table 11. Mineralogy of the Van Buren Sand, From Point-Count Data

Sample	Chert	Quartz	Feldspar	Other minerals
VB-1	17.2	68.6	12.4	1.8
VB-2	15	68	14.4	2.6

Modeling Results: APACC Model – Chert Content in Fine Sand

The calibration for the Van Buren sand was built with data from pure Ottawa quartz sand (Texas) and a reactive chert (Adameek Pit Chert, Texas). The calibration is quite good, with $r^2 = 0.9965$ (Figure 31). Table 12 presents the results of the analysis. Both

LIBS analyses of VB-1 and one analysis of VB-2 are good; one analysis of split VB-2 is quite high, probably because of the heterogeneity of the sample.

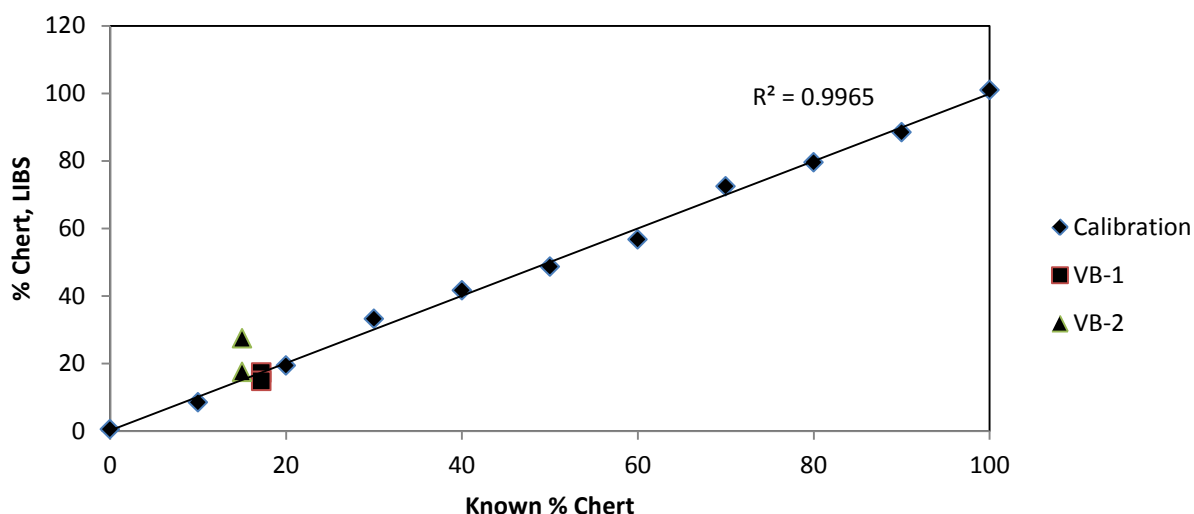


Figure 31 Calibration of chert-quartz model and analysis of chert in Van Buren sand.

Table 12. Results of Chert Analysis in Van Buren Sands

Sample	%Chert, LIBS	% Chert, Point Count	Absolute Error
VB-1	17.3	17.2	0.1
VB-1	14.8	17.2	-2.4
VB-2	17.5	15.0	2.5
VB-2	27.4	15.0	12.4

Modeling Procedures: APACF Model – Fe Content in Fine Sand

The calibration for the Muskogee sand was built with the Fe concentrations as analyzed by atomic absorption. Splits 2 and 3 (MR-2, MR-3, MA2, MA-3, ML2, and ML-3) were used for the analysis, assuming that split 3 would have the same Fe concentration as the other two. The first splits (MR-1, MA-1, and ML-1) were used to validate the model. Measured Fe concentrations are given in Table 13.

Table 13. Fe Concentrations in Splits of Muskogee Sand

Sample	Fe, wt. %
MR-1	0.69
MR-2	0.68
MR-3*	0.68
MA-1	0.17
MA-2	0.17
MA-3*	0.17
ML-1	0.08
ML-2	0.09
ML-3*	0.09
*assumed to be the same as the other splits	

Modeling Procedures: OKF Model – Fe Content in Fine Sand

The calibration curve is robust, with $r^2 = 0.993$ (Figure 32). Results are given in Table 14. Most of the analyses are within 0.01 wt% of the measured values, but as high as 0.08%. A larger number of calibration samples would improve the results.

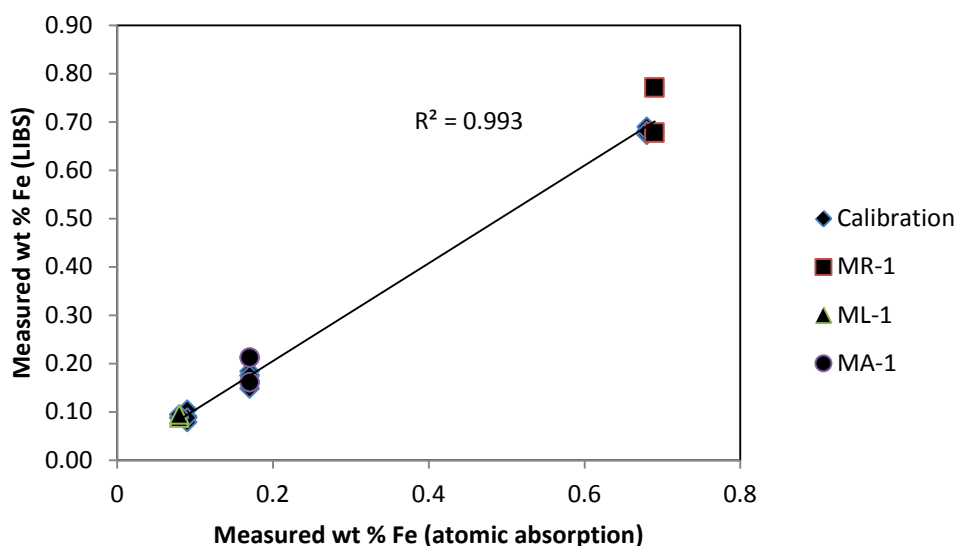


Figure 32 Fe calibration for Muskogee sand.

Table 14. Results of Fe Analysis, Muskogee Sand

Sample	Fe, wt. %, AA	Fe, wt. %, LIBS	absolute error
MR-1	0.69	0.68	0.01
MR-1	0.69	0.77	-0.08
MA-1	0.17	0.16	0.01
MA-1	0.17	0.21	-0.04
ML-1	0.08	0.09	-0.01
ML-1	0.08	0.09	-0.01

FINDINGS AND CONCLUSIONS

Research was conducted on the feasibility of using Laser Induced Breakdown Spectroscopy (LIBS) as a real-time construction aggregate monitoring system. In cooperation with NYSDOT, the KSDOT and TXDOT, aggregate samples were evaluated to determine whether laser-induced spectra could be modeled and correlated with known aggregate sources or known aggregate or engineering properties.

Research findings were as follows:

NYSDOT Findings

- The acid insoluble residue (AIR) content and percent carbonate rock (or silicate rock) in a silicate rock-carbonate blend were effectively predicted by a LIBS generated model. Using test samples received from NYSDOT, AIR predictions were within 1 to 2% of the analytical values provided by NYSDOT.
- Percent carbonate content in silicate rock-carbonate blends were effectively predicted within approximately 4 to 9% of the actual blended values.

KSDOT Findings

- The specific source bed of limestone aggregates extracted from one of 16 beds in three KSDOT quarries could be predicted by the model 100% of the time.
- Similarly, the expected results of KSDOT D-cracking tests could be predicted 100% of the time.

TXDOT Findings

- The percent of alkali-silica reactive chert, in a chert-quartz sand blend, could be predicted within a range of approximately 0.2% to 4.2% of the actual blended value.
- More and less reactive cherts could be properly classified with limited modeling data approximately 87% of the time.
- The identity of our different chert types (some reactive and some nonreactive) could be differentiated 100% of the time

APAC-Central Findings

- The percent chert in a fine aggregate (sand) could be predicted within a range of 2.5% using a calibration curve generated with quartz and sand from a different area. One sample with larger error indicates that sample heterogeneity is a problem and more laser shots should be taken to insure that the analyzed sample is representative. These results are additionally significant because it appears that calibrations might be transportable from one area to another (i.e., TX chert to APAC chert).
- The percent Fe in glass sand could be predicted to within 0.08 wt. %, even at relatively low concentrations (< 1 wt. %).

It was concluded from these findings that:

- Laser-induced spectra are unique to the specific aggregate material tested and contain significant information about the fundamental properties of aggregate material.
- Such spectra can be modeled using multivariate models and such models provide a means to generate regression equations that can effectively identify the specific spectral pattern associated with the target material.
- Remote laser monitoring using LIBS has the potential to generate a large number of samples and spectral data arrays, within a very short period of time and this feature is significant in concluding that such a technology offers real potential for its application as a quality control tool in aggregate processing systems.

PLANS FOR IMPLEMENTATION

Results of this research effort suggest that a laser-induced spectral emission can be modeled and correlated with aggregate sources and aggregate properties. The light emitted from the targeted aggregate material, if resolved, can uncover latent properties

of the material that conventional chemical and physical tests do not readily reveal. The subject technology has the potential to identify the aggregate source in real-time in the field without sample preparation. It provides a means to identify preapproved materials and ensure that only such materials are being introduced into the production process. It also provides a means to calibrate the spectral pattern against known engineering properties to determine whether the aggregate can be expected to pass or fail designated test criteria. Commercialization of the subject technology could provide State DOTs and material suppliers with a real time, nearly instantaneous aggregate characterization and quality control tool.

Furthermore, while the results presented in this report are based on discrete laser shots focus on individual aggregate particles, the frequency of laser firings can typically be set to range from 1 to 50 Hz (shots per second). As a result, it is possible to generate very large sample populations; for example thousands of analyses can be obtained in a few minutes. The combination of emission spectra with over 13,000 data points (i.e., variables) and the number of laser shots (i.e., samples) provide the means to generate models with unprecedented levels of information, especially when compared to the number of samples collected and tests conducted during conventional physical, chemical and mineralogical testing of aggregate, which is commonly in the single digits.

The authors of this report have initiated the development an automated real-time monitoring system that can be used to capture the data generated by a continuous firing laser system. This developmental process involves transitioning the LIBS process from an individual “particle to particle focusing and targeting system” to a “bulk material sampling and laser targeting system.” The objective of the patent pending Bulk Material Sampling and Laser Targeting (SLT) System under development is to provide a continuous or semi-continuous flow of aggregate passed a laser, to enable repeated firing at the target source. The planned system is composed of three major sub-systems: 1) a material flow system that provides for the flow of aggregate material passed a laser targeting point, 2) a laser targeting system (including dust suppression), and 3) the laser- optical system. A series of prototypes have already been fabricated.

Although the concept of employing a laser monitoring system for quality control purposes might at first glance appear to be readily adaptable to a field application, the practical application of transitioning from a laboratory based LIBS system to an industrial setting is not so straightforward. Industrial settings, and in particular an aggregate processing system, will almost certainly introduce non-uniform ablation conditions, unlike those experienced in laboratory systems. Such conditions can interfere with laser targeting and the laser to target focal length. Such interferences could significantly affect the intensities and induced spectral emission. In addition, the presence of dust and the atmospheric gas composition, including the humidity, in the vicinity of the laser induced ablation, could interfere with the laser energy reaching the targeted material and the light emitted during the ablation process. The laser and optical system must be segregated from the dust particles to prevent a buildup of dust in the system and corresponding operational difficulties. Finally, safety issues in a bulk material production environment demands that eye or skin exposure to operating

personal be avoided. Open and exposed targeting of materials in such an environment would be problematic.

The Research Team believes that the development of a viable field system will be successful. Plans have been initiated to develop a pooled fund study (KSDOT being the lead agency) to assist in making this transition.

It is of note that while a field system will not be capable of controlling all of the environmental conditions as precisely as a laboratory system and some poor spectra will result (due to factors such as poor focus and the simultaneous analysis of two grains), the robustness of a bulk monitoring process itself, in which hundreds or thousands of spectra will be collected, will permit the development of models that can average and smooth out the data to provide effective pattern recognition. This was already observed during the special-procedures testing of TXDOT sand samples described in the TXDOT Sample Analysis section (page 13). In this testing sand-sized cherts were placed in a shallow aluminum dish with vertical sides, and the dish was placed on the laser target platform, and randomly moved without focusing. This was done to see whether spectral data could be obtained to model the system. The results were positive and effective TXDOT chert and ASR identification models were developed.

REFERENCES

1. Esbenson, Kim H. *Multivariate Data Analysis – In Practice. An Introduction to multivariate data analysis and experimental design*. 5th edition, 598 sider. Camo Process AS, ISBN 82-993330-2-4
2. Cremers, D.A. and L. J. Radziemski, *Handbook of Laser- Induced Breakdown Spectroscopy*, Wiley, Hoboken, NJ, 2006.
3. Gottfried, Jennifer, R. Harmon, F.C. Delucia Jr, A.W. Miziolek. "Multivariate Analysis of Laser-Induced Breakdown Spectroscopy Chemical Signatures for Geomaterial Classification," *Spectrochimica Acta Part B* 64, 2009, pp. 1009-1019.
4. McManus, Catherine, N. McMillan, R. Harmon, R. Whitmore, F. Delucia and A. Milziolek. "The Use of Laser Induced Spectroscopy in the Determination of Gem Provenance: Beryls," *Applied Optics*, Vol. 47, Issue 31, pp. G72-G79, 2008.
5. McMillan, Nancy, C. Montoya and W.H. Chesner. "Correlation of Limestone Beds using Laser-Induced Breakdown Spectroscopy and Chemometric Analysis," *Applied Optics*, Vol. 51, Issue 7, B213-B222, 2012.
6. Spectroscopy On-Line, NASA to Use LIBS on Next Mars Rover
<http://www.spectroscopyonline.com/spectroscopy/article/articleDetail.jsp?id=658027>, 2010
7. Weritz, F., D. Schaurich, F. Weritz, H. Wiggense. "Laser Induced Breakdown Spectroscopy as a Tool for the Characterization and Sorting of Concrete Waste Material in View of Higher Order Re-Use," *Proceedings of the International Symposium on Non-Destructive Testing in Civil Engineering*, NDT-CE 2003, September 16-19, 2003, Berlin, Germany.

8. *Friction Aggregate Control and Test Procedures, Materials Method No.: NY 28*. New York State Department of Transportation, Materials Bureau, Albany, NY, July 2007.
9. *KDOT Construction Manual, Part V, Materials Tests*, Kansas Department of Transportation, Topeka, KS, 2010.
10. Multari, R. A., D.A. Cremers, J.M. Dupre and J.E. Gustafson. "The Use of Laser-Induced Breakdown Spectroscopy (LIBS) for Distinguishing between Bacterial Pathogen Species and Strains," *Applied Spectroscopy*, vol. 64, Society of Applied Spectroscopy, pp. 750–759, 2010.