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DEVELOPMENT AND DEMONSTRATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR IN-SITU, ON-LINE COAL ANALYSIS

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ABSTRACT

Coal characterization and prediction of slagging behavior has reached great relevance for coal-fired power plant operators; especially, for units subject to large fuel quality variability, fuel switching and coal blending. Laser-Induced Breakdown Spectroscopy (LIBS) and Artificial Neural Networks were used in the development of an on-line system for in-situ coal characterization. The system consists of an excitation Nd:YAG laser, an Echelle spectrometer, a photodiode/amplifier unit, supporting optics and a processing computer, for above-the-coal belt applications. Demonstration of the system was carried out at PPL Generation's Montour Power Station, to measure elemental composition of the plant coal supply, and the feedstock heating value and ash fusion temperature. A coal inventory composed of a range of twelve bituminous coals, fired at the station, was used to calibrate the system in the laboratory. The results demonstrated the capability of the LIBS technology to detect the following inorganic elements in real time: Al, C, Ca, K, Mg, Na, Fe, S, Si, and Ti. The measurement repeatability for heating value and initial deformation fusion temperature was within ± 76 Btu/lb and 33°F, respectively, for a range of heating values and fusion temperature from approximately 10,500-14,000 Btu/lb and 2,000-2,600°F,

respectively. The measurement system is supported by a processing software, which allows real-time display of the coal properties, and will provide expert advice to boiler operators for coordination of coal yard operation, and modification of boiler operation for efficient fuel combustion and mitigation of slagging and fouling.

INTRODUCTION

Coal-fired power plants in the US and worldwide face significant challenges due to unanticipated changes in feedstock characteristics. Coal characteristics can be variable with regard to total ash and moisture level, sulfur content, the composition of ash-forming inorganic material, and the concentration of trace impurities, such as chlorine. These characteristics have a direct impact on the calorific value of the coal, sulfur dioxide (SO_2) emissions, the ash fusion temperatures and coal slagging and fouling potential, and the risk of corrosion of boiler metal components; respectively. These characteristics can greatly vary depending upon coal rank, mine origin and, even, within a seam in a particular mine. For example, ash-forming inorganics, which cannot be economically removed before combustion, can range from below 3 percent in a "clean" coal feedstock to over 40 percent in some low-rank coals [1].

Coal yard and boiler operators are limited by the range of tools they have available to cope with high-levels of variability in coal composition, introduced naturally by geological circumstances or by coal changes resulting from seasonal adjustments in coal supply and reclaim. The most traditional methods used to evaluate the characteristics of fuel shipments or of blended coal sent to the power plant rely on standardized laboratory analysis (American Society for Testing and Materials, ASTM, Methods). However, a limitation of these methods is that they require sample preparation and their processing time (of the order of several days) for results to be obtained. The difficulty in obtaining real-time information on coal quality before it is burned results in the plant having to take mitigation actions on a retroactive basis. While ASTM techniques could be used to obtain a complete historical record of coal quality over long time periods, it would require a considerable amount of sample preparation and labor that would make this approach prohibitively complicated and expensive.

On-line coal analyzers are commercially available and have been in use for a few years in coal mines, washeries and coal-fired power plants. Most of the applications to power plants have been for blending to comply with emission regulations or to verify the quality of coal received. Mainly, these analyzers work on a nuclear source-based principle or X-Ray Fluorescence (XRF). The most used nuclear source-based technology utilizes a Prompt Gamma Neutron Activation Analysis (PGNAA) to provide continuous monitoring of coal composition. The PGNAA is suited for installation at the conveyor belt, but it requires an involved calibration procedure to account for variations in bed depth, and sample temperature and moisture content to provide accurate measurements [2]. The main drawbacks of the nuclear-based instruments are their large footprint and the requirements of the isotope source (permitting, handling, automatic compensation for source decay, and replenishing cost). The XRF-based instruments have not been as extensively deployed in coal-fired power plants as the nuclear-based instruments. The XRF technology can only measure elements with atomic numbers greater than 11 (sodium), needing the use of correlations for a full report of carbon, hydrogen and hydrogen content, and ash composition and heating value [3].

Recent developments in advanced laser-based methods have confirmed some maturity in technologies that could be used to determine coal elemental composition, which would be used in determining the properties of fuels "to-be-fired" in coal-fired boilers. One of these technologies is known as LIBS, or Laser-Induced Breakdown Spectroscopy. LIBS is a variation of plasma emission spectrometry in which the excitation is brought about by the output from a pulsed laser focused on the sample to be analyzed. The high electric field at the laser focal point causes electric breakdown, like a spark. The sample, or a portion of the sample, is vaporized during the laser pulse to form a plasma of the sample components, containing electronically excited atoms and ion of the species present in the sample. Light emitted from the plasma is collected and transmitted to a grating spectrometer, where the spectrum is recorded using intensified charge-coupled device arrays.

Emission lines from ions and atoms can be measured after approximately one microsecond of the spark, after the strong continuum background has decayed. The wavelengths of the lines in the emission spectrum identify the elements present, and the intensities of the line provide their concentrations. The emission intensity from the atomized species in the sample, with the assumption of uniform plasma temperature, can be described by the relationship:

$$I_i = A_i n \sum_j \left\{ g_i^{(j)} \exp\left(-\frac{E_i^{(j)}}{kT} \right) \right\} \qquad [1]$$

Where I_i ($J \cdot s^{-1}$) is the emission intensity of species *i*, A_i ($J \cdot m^3 \cdot s^{-1}$) is a variable which refers to species *i*, and it includes the transition probability, n_i (m^{-3}) represents the concentration of species *i*, $g_i^{(j)}$ is the statistical weight of species *i* at upper energy level *j*, $E_i^{(j)}$ is the upper energy level of species *i*, *k* ($J \cdot K^{-1}$) is the Boltzman constant and T (K) is the plasma temperature. The spectral information from LIBS is readily available for data calibration, and subsequent correlation using advance artificial intelligence (AI) tools.

LIBS can offer to coal-fired power plants the following opportunities:

- In-situ, above-the belt installation with minimal space requirements and ease of retrofit.
- On-line sampling and analysis of large volumetric flows of coal.
- Multi-elemental analysis for detection and reporting of mineral concentrations in the coal in just one measurement.
- Good trade-off between fast response time for statistical sampling and high accuracy.
- Capability of advanced signal processing for determination of high-order coal properties (such as heating value, fusion and viscosity temperature, slagging and fouling indices, and blend ratio).

A schematic of the LIBS concept for deployment in coal-fired power plants on an above-the-belt application is shown in Figure 1.

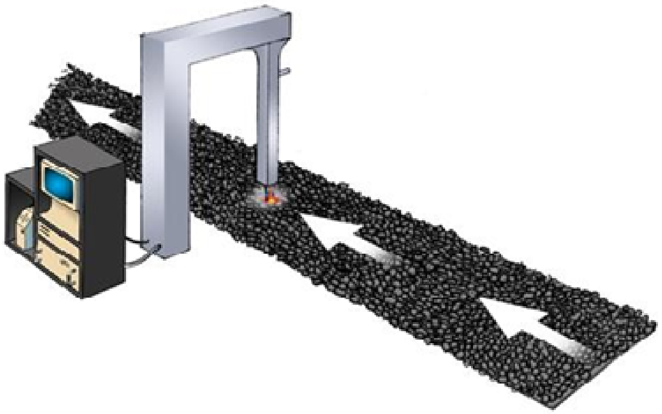


Figure 1. Schematic of LIBS Measurement System

This paper reports demonstration of a LIBS instrument and supporting software at PPL Generation's Montour Power Station. A full-scale LIBS system was built and tested/calibrated in the laboratory. The calibrated system was installed at Montour to analyze coal as it is transported on one of the transfer conveyor belts between the crushing station and the coal bunkers. The system was mainly evaluated in the field to determine its measurement accuracy and repeatability for determination of coal heating value and ash fusion temperature in real-time. The measurement repeatability achieved by the full-scale system for heating value and initial deformation fusion temperature was within ± 76 Btu/lb and 33°F, respectively, for a range of heating values and fusion temperature from approximately 10,500-14,000 Btu/lb and 2,000-2,600°F, respectively.

PLANT INSTALLATION

PPL Generation's Montour Station is located in Washingtonville, Pennsylvania. The plant has two 775 MW coal-fired units equipped with state-of-the art technology for nitrogen oxide (NO_x) and SO_2 control. Montour Station fires bituminous coals that arrive via rail trains from a range of suppliers. An important problem with the plant feedstock is the fuel variability and the delay in obtaining fuel analysis from the on-site laboratory, especially, when up to 50 percent of the unloaded coal goes directly to the boilers. Table 1 includes a list of the range of coals most commonly fired at Montour and their corresponding important fuel characteristics. Montour faces the increasingly difficult job of maximizing unit generation, while accessing a large number of suppliers to offset the increasing cost of fuel, and maintaining good unit availability by mitigating the undesirable impact of fuel quality variability on unit operation.

A full-scale LIBS system was assembled in the laboratory and tested with coal samples from Montour, to provide instrument preliminary calibration with known static samples. The LIBS system consists of an excitation laser, a spectrometer, ancillary optics components, and a processing computer. The selected optics allow for laser and plasma light to be conveyed by a unique set of lenses, and to provide enough depth of field to compensate for significant changes in the height of the moving coal layer, due to sagging of the conveyor belt. The system is capable of detecting with good accuracy and repeatability the following elements in real time: Al, C, Ca, K, Mg, Na, Fe, S, Si, and Ti.

Table 1. Characteristics of Coals Fired at Montour Power Station

Coal	IDT (deg. F)	HHV (Btu/lb, db)	Fe2O3 (ash %)	S (%, dry)
Coal A	2,069	13,298	25.93	2.99
Coal B	2,162	13,933	17.68	2.20
Coal C	2,253	12,844	17.44	2.38
Coal D	2,121	13,928	18.51	2.60
Coal E	2,121	14,027	21.27	2.55
Coal F	2,149	13,814	17.45	1.84
Coal A-B Seam	2,757	14,013	15.82	1.59
Coal A-Crop	2,573	10,934	7.77	0.64
Coal A-D Seam	2,003	13,506	32.90	4.23
Coal C-Bottom B	2,618	10,486	13.61	3.16
Coal G	2,042	13,597	19.75	2.66
50% Coal C/50% Coal C-Bottom B	2,435	11,665	15.52	2.77
67% Coal C/33% Coal A-Crop	2,298	12,213	14.24	1.80

The concept for the LIBS system reported in this paper consists of the LIBS measurement equipment and associated software for system operation/control, modeling and determination of sample elemental composition, as well as other parameters, such as heating value, fusion temperature and blend ratio (when blending of different coals), and data interface. Model development and calibration of the LIBS data is done using artificial neural networks (ANN's). System calibration was performed to compensate for those variables that affect the intensity of the LIBS signal, and to be used as a reference to check the integrity of the system after installation in the field. The samples of coals included in Table 1 and provided by Montour were used as calibration standards. These samples covered an expanded range of analyte concentrations expected in the field demonstration. This allows for calibration of the system for any expected coals at a particular customer site. The calibration samples were characterized using standard ASTM analysis. The concept used in the reported LIBS system is shown in Figure 2. An expert system block is also shown in Figure 2. The function of the expert system is to equip the LIBS system with an interface with the plant control system and provide expert advice to the plant engineers on coal yard and unit operation.

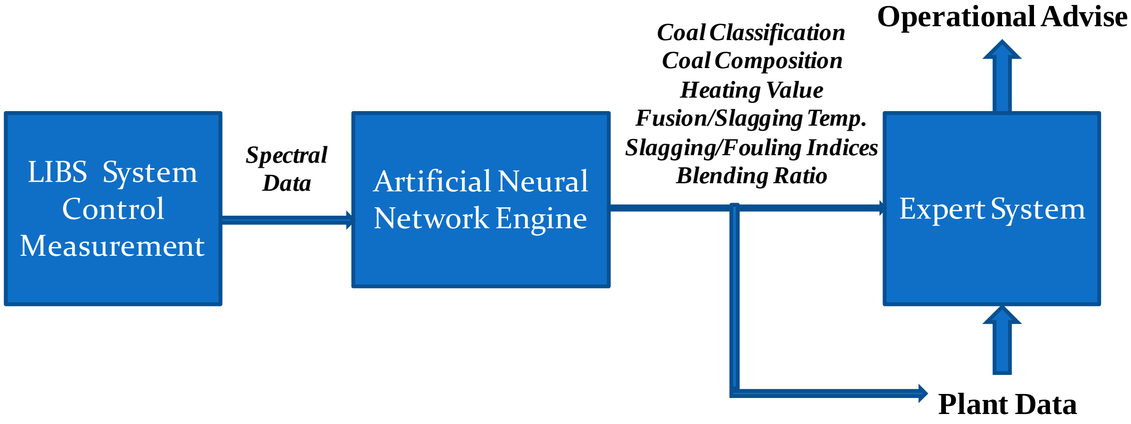


Figure 2. LIBS System Concept

The LIBS system was installed on one of the transfer conveyor belts between the crushing station and the coal bunkers. This installation point was chosen to avoid the need of mechanical samplers and compensate for the surface measurement-nature of the LIBS technology. Thus, the LIBS system was installed after a transfer point, on a 36 inch wide belt; where a mixed coal stream is presented to the analyzer with a coal top-size of no more than 2 inches. The belt speed in this application is 500 ft/min. Figures 3 and 4 show pictures of the system installed at PPL Generation's Montour Station. Figure 3 shows the LIBS probe installed on top of the 7B-Conveyor, the cabin built for the demonstration and the tip of the probe. The sensor head is suspended above the belt on the tripper floor. The electronic components (laser, spectrometer, control computer, etc.) were located in a positively pressurized, climate-controlled room above the conveyor. Figure 4 shows some of the components in the climate-controlled cabin, particularly, the laser head, the spectrometer box and the cabinet hosting the data acquisition, analysis and communication components. Analysis data are provided to plant engineers and in the future, via the Distributed Control System (DCS) data highway, in tabular and graphical form. This provides trend information, as well as time-stamped data for further analysis. A typical application screen is shown in Figure 5. The application screens can be customized to the specifics of each particular application. Additional application screens may include expert advice to coal yard and control rooms on actions to take for fuel blending, boiler control settings modifications, and implementation of optimal sootblowing schedules.

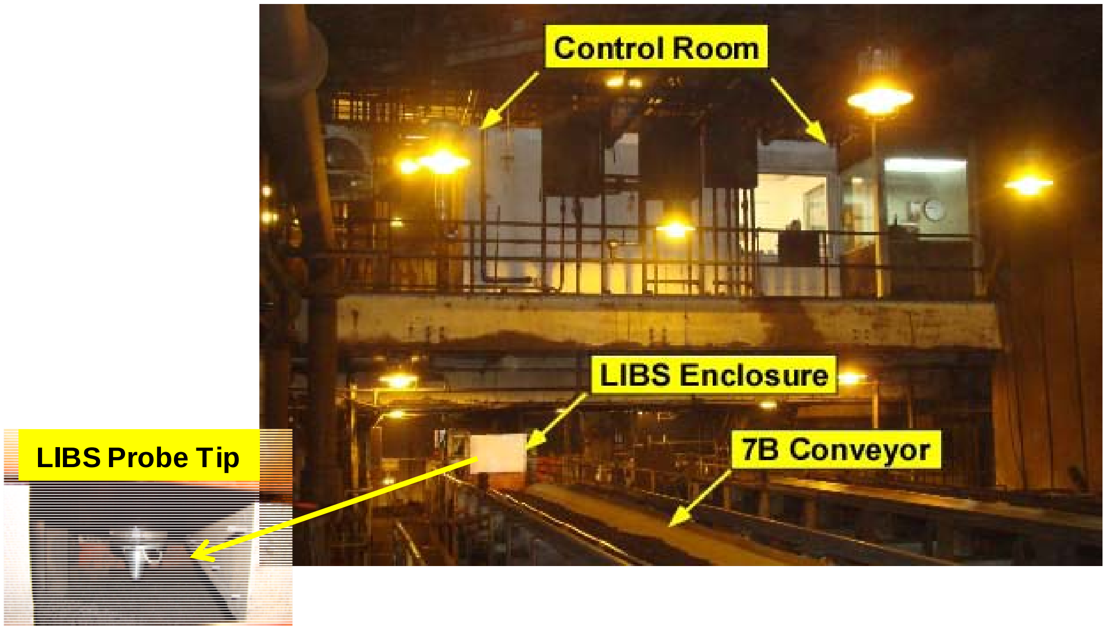


Figure 3. Photo of LIBS Belt-Mounted System

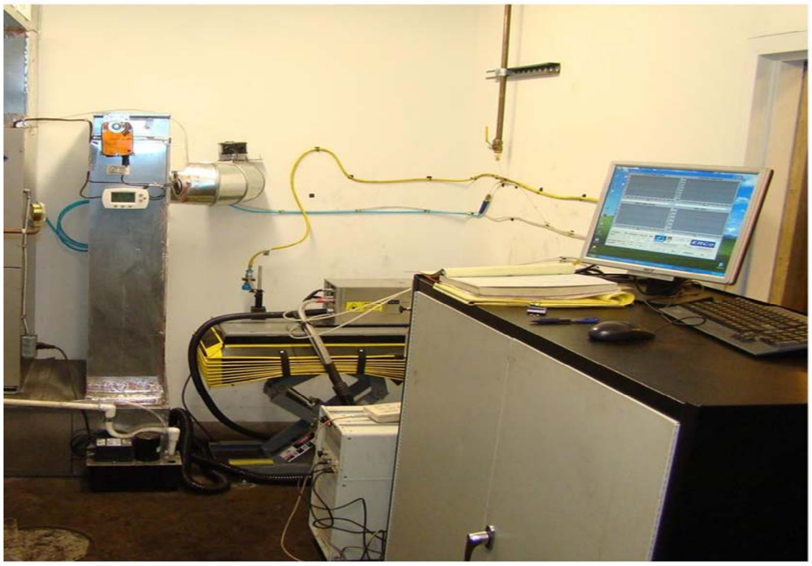
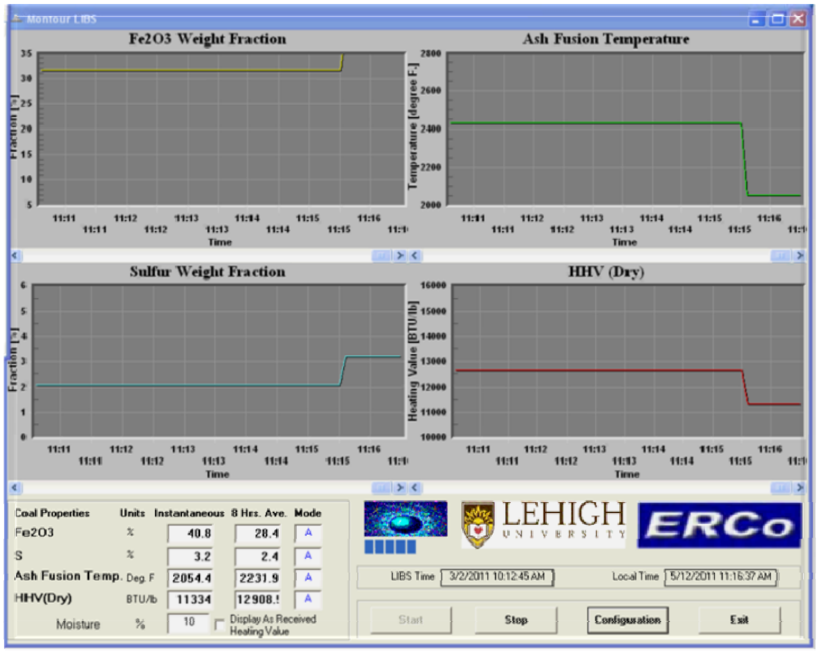


Figure 4. Photo of LIBS Components in Climate-Controlled Cabin



Coal Properties	Units	Instantaneous	8 Hrs. Ave.	Mode
Fe2O3	%	40.8	28.4	A
S	%	3.2	2.4	A
Ash Fusion Temp.	Deg. F	2054.4	2231.9	A
HHV(Dry)	BTU/lb	11334	12908.!	A
Moisture	%	10	☐ Display As Received Heating Value	

LIBS Time 3/2/2011 10:12:45 AM

Local Time 5/12/2011 11:16:37 AM

Figure 5. LIBS System Primary Operator Interface Screen

RESULTS AND DISCUSSION

Evaluation of the LIBS system at PPL Generation's Montour took place from January to March, 2011. Seventy-three hours of run time were conducted with the LIBS system in-service to evaluate the performance of the analyzer and associated software on its analysis of iron, sulfur, and heating value and initial deformation fusion temperature. Iron is of interest since elevated concentrations of this alkali promote reductions in the minimal ash fusibility temperatures. Sulfur is of interest, since that power plant desulfurization schemes require this input for optimal, cost-effective operation of SO_2 reduction systems. Six of the coals from Table 1 were scheduled for the verification period. Those coals correspond to Coals A, B, C, D, E and H in Table 1.

Although, a preliminary calibration was performed on the LIBS system in the laboratory, additional calibration was performed in the field. The calibration algorithm or ANN models were updated using data from a dynamically running material dataset. The field calibration allows additional coals to be included in the calibration set that the customer may want to include in the portfolio of coals to be burn at the station. LIBS data for calibration and verification were collected at a laser pulse frequency of 5 pulses per second. The typical collection time per data point was of the order of 10 minutes; however, the analyzer can be adjusted to report analysis every minute at expense of measurement accuracy. It should be mentioned that during the on-line data collection and analysis, the LIBS software examines the spectrum from each pulse and determines the adequacy of the information, discarding spectral data that correspond, for example, to ice or water in the sample, or pure pyrite, etc.

Validation tests were run to evaluate the accuracy and precision of the on-line coal analyzer, as well as to identify limitations of the system under dynamic measurement conditions. The validation tests consisted of grabbing reference coal samples using a conventional method, followed by proper laboratory analysis, and comparing the laboratory results with the data collected and analyzed by the LIBS system. Reference samples were analyzed for heating value, initial deformation fusion temperature (under reducing environment), total sulphur and iron oxide content in the ash, by G and C Coal Analysis Laboratory, in Summerville, Pennsylvania. Care was taken to ensure good synchronization of both the LIBS and the reference sampling. The two sampling and analysis methods are different in nature and completely independent. The grab samples were obtained from the running conveyor belt at 10-minute intervals, following ASTM D-2234 procedures. This sampling method was preferred than using a "stopped belt" cut approach, to avoid disruption to the plant coal loading operation. A total of 120 samples, over the duration of the tests with six different coals, were obtained for comparison. This number of samples is in excess of the 60 comparisons required by the ASTM D-6543 Guide [4] for evaluation of measurements made by on-line coal analyzers.

Results of the validation tests are shown in Figures 6 to 9 for heating value, initial deformation temperature, sulfur and iron, respectively. The heating value numbers are referred to a dry basis. The iron numbers are percentages in the ash. Two sets of data are included in those figures. The first set, identified as LIBS Results-1 corresponds to a unique ANN model developed for all the calibrated coals. This model uses a feed-forward network architecture. The ANN's were trained using standard back-propagation algorithms with minimization of the training error below 0.015. The second set, identified as LIBS Results-2 corresponds to predictions from advanced algorithms based on Kohonen unsupervised ANN's. As it can be seen from Figures 6 to 9, the LIBS reported data closely follow the trend determined by the reference analytical method, with the unsupervised ANN calibration model resulting in reduced scattering in the measurements.

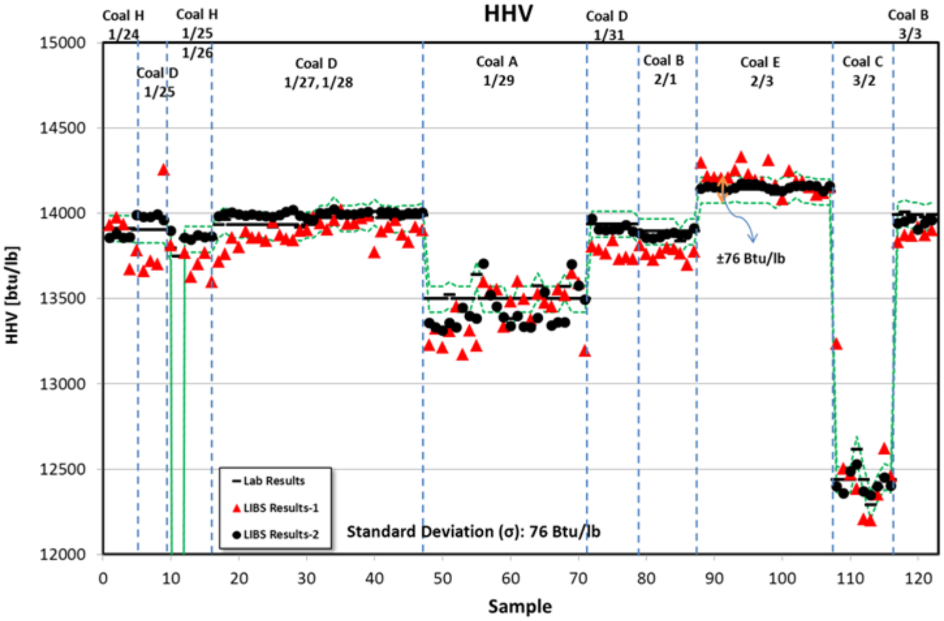


Figure 6. LIBS and Laboratory Results for Higher Heating Value

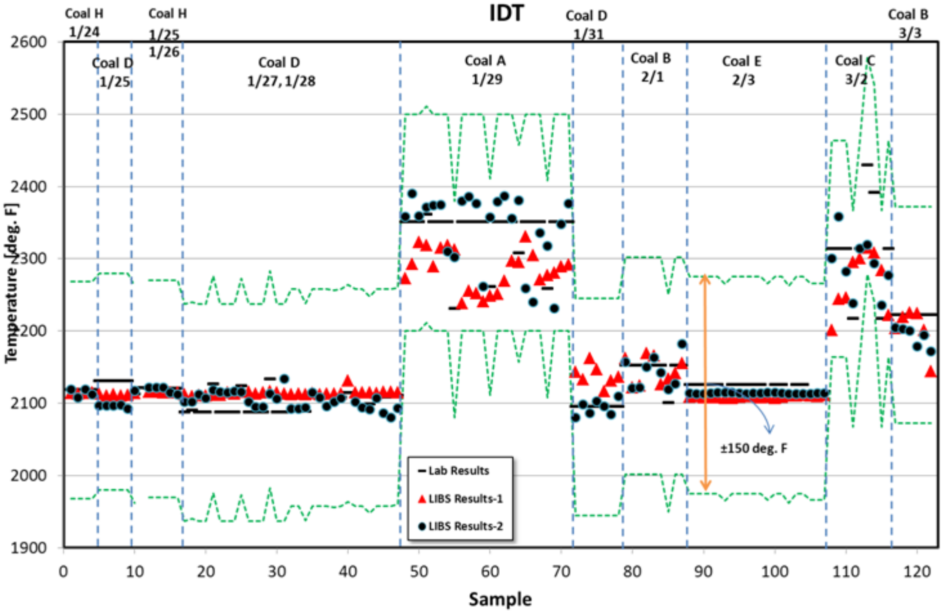


Figure 7. LIBS and Laboratory Results for Fusion Temperature

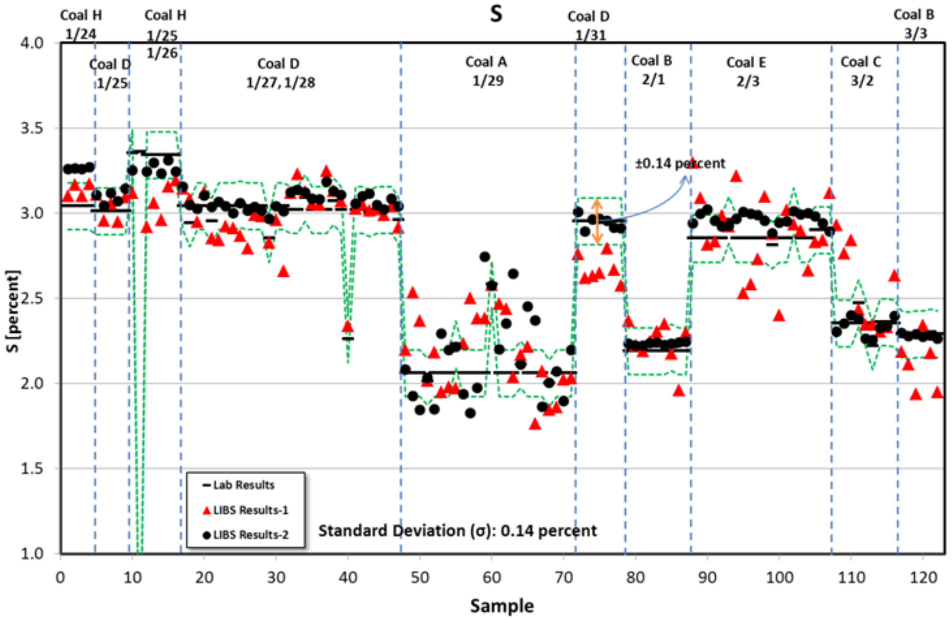


Figure 8. LIBS and Laboratory Results for Sulfur Content

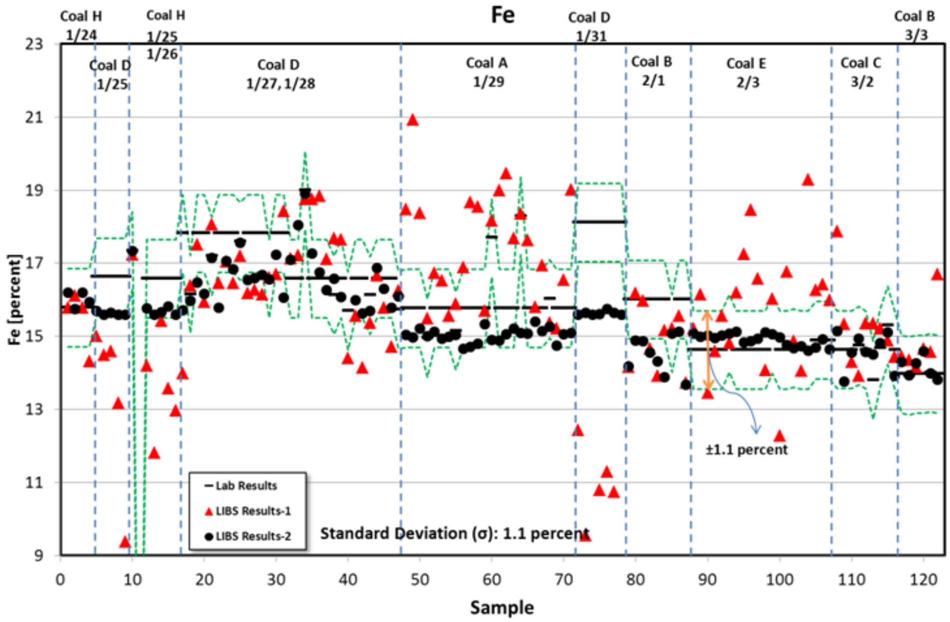


Figure 9. LIBS and Laboratory Results for Iron Content

A statistical analysis was performed on the data, using the guidelines provided by the ASTM D-6543 Method. Table 2 includes the values of the root mean squared difference (RMSD) between the reference and the analyzer values, as well as the Grubbs' indices of measurement precision for the coals most commonly used by PPL Generation at Montour. The RMSD values were calculated using RMSD = $[\Sigma (x_i – y_i)^2 / n]$. Where x_i, y_i and n are the analyzer value in the *i*th comparison, the reference value in the *i*th comparison, and the number of paired comparisons, respectively. Smaller RMSD statistics implies a precise analyzer, with small bias being evaluated by a fairly precise reference method. The Grubbs' estimator of measurement precision is typically used with two independent reference methods, and it is an unbiased one-sigma precision estimate. In the evaluation reported here, only one set of independent reference measurements were used. The statistics of the Grubbs' estimator still applies, and it reports the precision of the LIBS system in relation to the variance of the errors of the measurements made by the analyzer. These values of precision compare very well with the reported ASTM maximum expected reproducibility levels for those parameters, which stand at 0.70 percent, 0.15 percent, 150°F and 100 Btu/lb, respectively [5]. The results of Table 2 show a high level of accuracy and exceptional precision, comparable to reported similar statistics by the nuclear and XRF technologies. The relative measurement accuracy for iron, sulphur, fusion temperature, and heating value is ± 6.7, 5.1, 1.5 and 0.6 percent, respectively. The relative precision for iron, sulphur, fusion temperature, and heating value is ± 5.6, 4.9, 1.5 and 0.6 percent, respectively. The reported relative values of accuracy and precision are referred to the averaged values for the entire dataset, which is composed of a range of coals with distinct values for each of the parameters.

Table 2. Statistics of LIBS Measurement Accuracy and Precision

	RMSD Accuracy	Grubbs' Estimator of Precision
Iron (%)	1.07	0.90
Sulfur (%)	0.14	0.13
Fusion Temp. (°F)	33.16	32.98
Heating Value (Btu/lb)	75.86	75.98

CONCLUSIONS

A full-scale LIBS system was developed and validated at PPL Generation's Montour Power Station. The LIBS system works on a concept that utilizes plasma emission spectrometry and artificial intelligence for probe calibration and coal data correlation. The project goals were met and very favorable results were achieved in terms of demonstrating the capability of a LIBS-based system to work on-line, on a "top-of-conveyor-belt" installation, as well as good measurement statistics. The system was capable of detecting the following elements in real time: Al, C, Ca, K, Mg, Na, Fe, S, Si, and Ti. The validation of the data showed very good accuracy and repeatability for iron, sulfur, fusion temperature and heating value. The average RMSD value for a range of six bituminous coals, most commonly fired at Montour was of 1.07 percent, 0.14 percent, 33.16°F, and 75.86 Btu/lb for iron, sulfur, fusion temperature and coal heating value, respectively. The average Grubbs' estimator of measurement precision was of 0.90 percent, 0.13 percent, 32.98°F, and 75.98 Btu/lb for iron, sulfur, fusion temperature and coal heating value, respectively. At a projected cost, lower than competing technologies for on-line coal measurements, LIBS will offer a strong justification for installation in coal-fired power plants.

ACKNOWLEDGMENTS

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REFERENCES

1. Romero, C., De Saro, R., Craparo, J., Weisberg, A., Moreno, R. And Yao, Z. "Laser-Induced Breakdown Spectroscopy for Coal Characterization and Assessing Slagging Propensity." Energy & Fuels 2010, 24, 510-517.
2. Foster, S. "What is Involved in Effective Calibration of a PGNA Analyzer in the Factory and the Field," Int. On-Line Coal Analyzer Technology Conference, St. Louis, Missouri, November 8-10, 2004.
3. InduTech, OXEA Online X-Ray Elemental Analyzer, www.indutech.com, 2011.
4. ASTM D-6543, "Standard Guide to the Evaluation of Measurements Made by On-Line Coal Analyzers." ASTM International, May 2000.
5. Drbal, L., Boston, P. and Westra, K. "Power Plant Engineering." Black & Veatch, Springer, 1996.