Laser-Induced Breakdown Spectroscopy for Coal Characterization and Assessing Slagging Propensity

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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 neural networks were used to characterize elemental composition of coal samples and estimate the initial deformation ash fusion temperature. A coal inventory was assembled with a range of slagging characteristics and fusion temperatures from 955 to 1480 °C. The following inorganic elements were measured in the laboratory: Al, Ca, K, Mg, Na, Fe, Si, and Ti, and correlated to coal ash initial deformation fusion temperature under reducing conditions. The LIBS system achieved elemental composition measurement accuracy within ±15% (absolute). The LIBS system was tested off-line at a power plant on three different coals. The field results indicate an average relative fusion temperature prediction error when compared to American Society for Testing and Materials (ASTM) standardized measurements of ±56 °C, and an average precision for the LIBS measurements of ±14 °C.

1. Introduction

Stringent sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emission limits, and economic competition in an unregulated power generation market in the U.S. have forced coal-fired plants that fire a specified type of Eastern US bituminous coals to fire coals and fuel blends with different characteristics than the design coals. Hence, there has been a recent growth in the international trade with foreign coals, and the use of Western US, low-sulfur coals to replace high-sulfur Eastern US bituminous coals. However, there are some detrimental effects associated with these off-design coals. For example, milling capacity may become limited when converting to off-design fuels, due to the greater tonnage of coal required and often higher moisture content. Other constraints, while less obvious, still have an impact on unit operation and availability (due to reduced generation output and unplanned shut-downs). These include, for example, increased stack opacity spiking due to the lack of inherent SO_3 conditioning for efficient electrostatic precipitator (ESP) performance, and the development of slagging/fouling conditions. Particularly, unexpected and/or uncontrolled slagging deposits on the boiler high-temperature surfaces can develop and interfere with heat transfer, reduce steam temperatures, increase fuel firing rates and fan power (to overcome larger pressure drops in the convective pass), and reduce thermal efficiency.[1] Additionally, deposits that grow from partially blocking the spacing between tube banks to form clinkers often lead to increased gas velocities, erosion, and major incidents of internal boiler damage due to large fused ash material falling to the bottom of the boiler. Corrosion may also occur underneath these deposits.

All coals have a significant content of ash-forming inorganic material, which cannot be economically removed before combustion. This amount can range from below 3% in a "clean" coal feedstock to over 40% in some low-rank coals. The behavior of mineral matter in the coal is complex and depends on the interactions between the forming deposits, the flue gas, and heat transfer equipment, and it may lead to slagging conditions. Slagging refers to deposits within the furnace, in areas directly exposed to flame radiation (waterwalls and spaced pendant superheaters). Slagging problems are aggravated with off-design coals when upper furnace flue gas temperature levels are elevated. The combination of higher flue gas temperatures and ash with lower ash fusion temperatures increases the risk of plastic ash formation and slagging in coal-fired boilers on the close-to-the-furnace heat transfer surfaces, such as superheater screen tubes and boiler arch.

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 parameters used to evaluate the behavior of coal ash inorganics, and their possible effects on deposition on the furnace walls and high-temperature convective pass surfaces are laboratory analysis of the ash and standardized ash fusibility temperatures (American Society for Testing and Materials, ASTM Method D6349 (typically) and D1857, respectively).[2] However, a limitation of these techniques is that they require

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(1) Romero, C.; Sarunac, N.; Levy, E. *Sootblowing Optimization in Coal-Fired Boilers.* Twenty-Sixth International Technical Conference on coal Utilization and Fuel Systems, Florida, March 2001.

(2) (a) ASTM Standard D6349. Standard Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Couple Plasma − Atomic Emission Spectrometry, DOI: 10.1520/D6349-08E01; (b) ASTM Standard D1857. Standard Test Method for Fusibility of Coal and Coke Ash, DOI: 10.1520/D1857-87R00; ASTM International: West Conshohocken, PA, 2000; www.astm.org.

sample preparation as well as their processing time (of the order of hours for processing and a couple of days for power plants to obtain results from outside laboratories) for results to be obtained. The analysis of ash-forming components is carried out in the laboratory, and it is not possible to get real-time information on coal quality before it is burned by only using these techniques. As a consequence, ASTM analysis can only suggest proper slagging remedial 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.

The parameter that is often used to specify fuel supply with regard to slagging propensity is the ash fusion temperature. The ash fusion test measures the softening and melting behavior of ash in a temperature range between 1050 and 1650 °C under either oxidizing or reducing conditions. This procedure involves determining the profiles of cone-shaped samples in terms of its initial deformation temperature, softening temperature (when the sample height equals the sample width), hemispherical temperature (when the sample height equals one-half the sample width), and the fluid temperature. Under reducing conditions, the fusion temperatures are lower (for most of the fuels), since the iron is present as ferrous ions, which have a greater fluxing action than when the iron is in the ferric form, under oxidizing conditions. The shortcoming of this approach is that it is performed off-line, in the laboratory, and it has an inherent tolerance on the measurement for repeatability and reproducibility as large as 80 °C.

Although, the application of coal ash fusion temperature based on laboratory analysis have proved useful in providing specifications for fuel acquisition and blending, real-time information on coal composition and predictive slagging potential (using this information) is in critical need. Online coal analyzers have been in use for a few years in coal mines, washeries, and, on a limited basis, in 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. There are a handful of commercially available real-time coal analyzers in the market nowadays. 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, sample temperature, and moisture content to provide accurate measurements.[3] The response time of this technology is typically on the order of 1 min, with a reported accuracy of better than ±2.0% for ash single elements. The main drawbacks of the nuclear-based instrument 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

coal and ash composition and heating value. Typical response time of the XRF-based instruments is on the order of 1.5 min. Reported accuracies for the XRF technology can be as high as ±1.5%.

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 predicting slagging propensity 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 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 and atomized 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 found after 500−1000 ns of the spark, with emissions lines superimposed on the strong continuum background. The wavelengths of the lines in the emission spectrum identify the elements present, and the intensities of the line provide their concentrations, after calibration in the laboratory. Calibration of the LIBS signals is necessary for quantitative analysis. The emission intensity from the atomized species in the sample, with the assumption of uniform plasma temperature, can be described by the relationship:

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

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, included 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 Boltzmann constant, and T (K) is the plasma temperature. This equation illustrates the direct relationship between elemental concentration and the electromagnetic intensity at different wavelengths in the plasma.

A detailed description of LIBS fundamentals and applications can be found in published references.[4,5] High sensitivity, rapid time response, and the capability for in situ measurements make LIBS an attractive technique for in situ coal-fired applications. LIBS has the ability to detect low-atomic number elements that are difficult to detect using alternative direct analysis techniques for solid samples.

Chadwick et al., have demonstrated the potential of LIBS for determination of elemental composition of lignite coals.[6,7] The results in refs 6 and 7 indicate detection limits for major inorganic elements in coal on the order of 0.01% by weight, and measurement repeatability and accuracy within ±10% absolute. Noda et al., applied the LIBS technique for

(3) Foster, S. *What is Involved in Effective Calibration of a PGNA Analyzer in the Factory and the Field*, International On-Line Coal Analyzer Tech. Conference, St. Louis, Missouri, November 8−10, 2004.
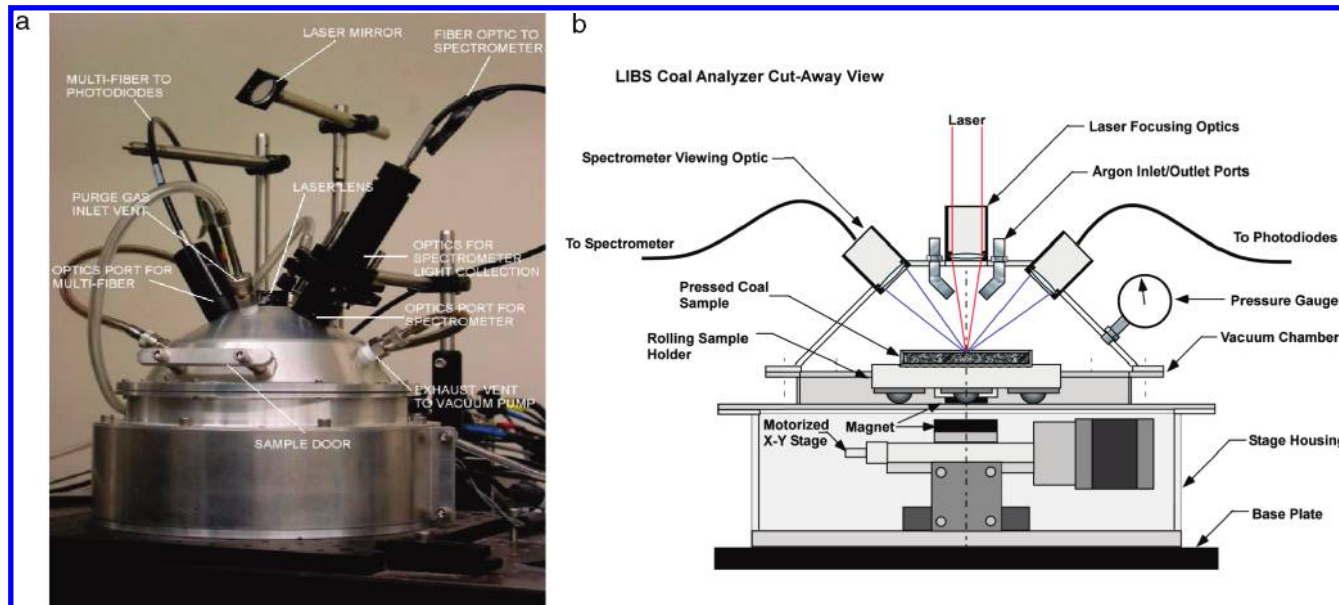
(4) Cremers, D.; Radziemski, L. *Handbook of Laser-Induced Breakdown Spectroscopy*; Wiley: New York, 2006.

(5) Miziolek, A.; Paleschi, V.; Schechter, I. *Laser Induced Breakdown Spectroscopy: Fundamentals and Applications*; Cambridge University Press: 2006.

(6) Body, D. Chadwick, B. *Rev. Sci. Instrum.* **2001**, *72*, 1625−1629.

(7) Chadwick, B.; Body, D. *Appl. Spectrosc.* **2002**, *56*, 70−74.

Figure 1. (a) Sample chamber. (b) Diagram of sample chamber.

detection of carbon content in fly ash, char, and pulverized coal under high-pressure and -temperature conditions, with good results.[8] Ottesen et al., used a LIBS-based system to characterize coal particulates in combustion environments, in situ and online.[9,10] Measurements of Mg, Ca, Al, Si, Fe, and Ti, relative to carbon, are reported in refs 9 and 10 for four coals of different rank and mineral content. The variability in the measurement results obtained in ref 10 was in the range from 0.03 to 1.68, expressed by a coefficient of variation, σ/μ (where σ is one standard deviation, and μ is the mean value of composition). This compares to a coefficient of variation of $\pm 3\%$ obtained with standard chemical analyses. Most recently, Gaft et al., reported on an online LIBS system for coal ash analysis, deployed over a four-month period on a moving plant conveyor belt.[11] Good data correlation (at least $\pm 0.5\%$ mean absolute error) for carbon, Fe, Mg, Ca, Na, Si, Al, Ti, and K and total ash was reported, in comparison to a PGNAA instrument run side-by-side to the LIBS system. Most recent reports on LIBS analysis applied to coal and ash can be found in refs 12−16

This paper reports the results of work performed and assess the feasibility of a concept that combines the LIBS technology, for coal ash composition detection, with artificial intelligence (AI) techniques to estimate coal slagging potential via prediction of the initial deformation ash fusion temperatur. This approach, working in situ and online, would provide advice to boiler operators on necessary operational measurements to anticipate and compensate for high-temperature ash deposition problems. The concept described in this paper evolved in steps that consisted of LIBS system

development and integration, LIBS system testing in the laboratory using simulated coal samples and on a broad set of coal samples, development of AI models, and LIBS system demonstration at a coal-fired power plant. All of the LIBS testing was performed using batch samples from a coal bank consisting of 16 coal samples, from power plant grab samples, and samples extracted from the coal pipes, for three different feedstock. The results achieved from this study demonstrated the merit of this concept for online monitoring of coal composition and real-time expert advice on high-temperature coal slagging potential and mitigation measurements. The mitigation measurements can have the following potential benefits: (1) Coal yard operators can be alerted on potential coal quality problems and make important decisions on blending, routing (to particular units), and rejection of fuels. (2) Boiler operators can be alerted of potential coal quality problems and anticipate and modify unit operation (per expert advice) to mitigate and prevent adverse slagging conditions, considering the trade-off between boiler fouling, stack emissions, and unit heat rate. (3) Boiler operators can be alerted of potential coal quality problems and start an aggressive sootblowing schedule for slagging control, considering the trade-off between boiler cleanliness and soot-blowing-related maintenance (such as steam or air consumption and tube erosion due to overblowing).

2. Experimental Section

The experimental apparatus used in this study is illustrated in Figure 1, panels a and b. The experimental LIBS setup was designed to accomplish: sparking of the sample with the laser under a controlled atmosphere, displacement of the sample to obtain a collection of shots, resolution of the spectra using a spectrometer and photodiode assembly, and processing of the acquired data.

The optical setup consists of an excitation Nd:YAG (neodymium-doped yttrium aluminum garnet) laser, a sample chamber, optical spectrometer, a photodiode/amplifier unit, and processing computer. The laser used in the LIBS system is a Q-switched Nd:YAG laser (Big Sky Laser, CFR-400), which yields coincident ultraviolet (UV), visible, and near-infrared (IR) 10 ns pulses, at a repetition rate of 10 Hz. The UV pulses were not used and were directed into a beam dump by a 266 nm

(8) Noda, M. *Spectrochim. Acta. Part B* **2002,** *57,* 701−709.
(9) Ottesen, D. *Appl. Spectrosc.* **1989,** *43,* 967−976.
(10) Ottesen, D. *Energy Fuels* **1991,** *5,* 304−312.
(11) Gaft, M. *Spectrochim. Acta Part B* **2008,** *63,* 1177−1182.
(12) Yu, L. *Plasma Sci. Technol.* **2005,** *7,* 3041−3044.
(13) Wu, G.; Lu, J.; Yu, L.; Chen, W. *J. Eng. Thermal Energy Power* **2005,** *20,* 365−368.
(14) Mateo, M.; Nicolas, G.; Yañez, A. *Appl. Surf. Sci.* **2007,** *254,* 868−872.
(15) Zhang, L. *Appl. Spectrosc.* **2008,** *62,* 458−463.
(16) Mateo, M. *Laser-Induced Breakdown Spectroscopy* (*LIBS*): *Applications to Combustion Related Processes in Laser Diagnostics in Combustion.* Lackner, M., Ed.; Processing Engineering GmbH: 2009.

Table 1. Compounds Used in Synthetic Coal Samples

		compound used in surrogate	
metal	oxide	name	formula
Si	SiO_2	silica	SiO_2
Al	Al_2O_3	alumina	Al_2O_3
Ti	TiO_2	titanium(IV) oxide	TiO_2
Fe	Fe_2O_3	iron(III) oxide	Fe_2O_3
Ca	CaO	calcium carbonate	$CaCO_3$
Mg	MgO	magnesium carbonate tetrahydrate	$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$
K	K_2O	potassium bromide	KBr
Na	Na_2O	sodium chloride	NaCl

beam splitter. This helped to focus the laser beams into a common focal point, making the sparks more repeatable. The visible and near IR pulses were directed down into the chamber by 1064 and 532 nm laser mirrors. Pulse energies of 100 mJ at 1064 nm and 180 mJ at 532 nm were used to generate the laser sparks on the sample. A $f/4$ lens is used to focus the light pulses onto the surface of the coal sample to create the LIBS spark.

The sample chamber is composed of two pieces machined from aluminum. The chamber encloses a sample cart, coupled to a motorized XY stage. The sample cart was positioned during measurements via a controller activated by the MeasureSolid software. The sample chamber allows a controllable nonoxygen atmosphere (helium was used) to preserve the sample integrity from the elements in air. Light collection elements used in this setup include $f/2$ mini-lenses to focus the emitting light, UV, and visible-grade fused-silica optical fibers, and two silicon photodiodes. An Echelle spectrometer (ESA, 3000 LLA) was used to collect the spectra data. This spectrometer contains an Echelle-type grating that allows for high resolution spectra to be collected over a broad wavelength range of 200−780 nm. The following elements were measured with the Echelle spectrometer: Al, Ca, Mg, Na, Fe, Si, and Ti. The timing window for the Echelle spectra collection was set by the MeasureSolid software. Additionally, a photodiode/amplifier assembly (ThorLabs, PDA55-switchable gain amplified silicon detector) was used to collect intensity traces for the emission lines of K (filter centered at 769.9 nm), as well as the background intensity of the plasma as a function time (filter centered at 821.0 nm).

For the synthetic coal experiments, a base mixture of anthracene (C_4H_{10}) was used in combination with selected compounds. Anthracene was selected as the base material because it has an appropriate H/C ratio and coarse power consistency. Compounds were selected to bring the targeted elements into the anthracene base, based on their chemical stability and easy dispersion into the anthracene. Silica, alumina, titanium oxide, iron oxide, magnesium carbonate tetrahydrate, potassium bromide, sodium chloride, and calcium carbonate were used as compounds to prepare the surrogate. Table 1 lists the compounds and their formulas used in the preparation of synthetic samples.

For the experiments with coal samples, a coal bank was assembled from 16 coals gathered from different coal-fired power plants. The coals in the coal bank include bituminous and lignitic type of ashes, with bituminous and sub-bituminous coals from the U. S., Russia, Indonesia, and South America. Samples were split and analyzed per ASTM procedures for elemental composition and ash fusion temperatures. Ash fusion temperatures were determined under a reducing environment, because it is the condition that typically produces lower fusion temperature. The range of initial deformation ash fusion temperatures for the coal inventory is from 955 to 1480 °C. A set of three samples was prepared and tested for each coal, after splitting the samples with a riffler. Riffled powdered samples were crushed to 60 mesh (250 µm) and dried. Samples on the order of less than a gram were spread on double-sided sticky tapes and placed on aluminum sample holders. This method was selected over other methods,

such as pressing the powders into pellets, and provided satisfactory results.[17]

Sixty laser pulses were used in a 6×10 matrix during each sample measurement. The spectral intensity data collected for each sample was processed to obtain LIBS intensity ratios. The acquisition cycle per sample included preparing and moving the sample, firing the LIBS system, and storing the resulting spectrum from each spectrometer channel and photodiodes. The Measure-Solid software was used to externally control the gating of the spectrometer and photodiodes. Time-gated optical detection is critical in optimizing signal response in LIBS experiments. Different delay and integration times were tried. The best configuration obtained for the experiments was a 1 µs delay time and a 3.5 µs gating time.

3. Data Processing

The data were processed using peak integration, background correction, ratio-to-normalization parameters (such as UV laser energy), and averaging of spectral data for each particular sample. This procedure allowed normalization for pulse-to-pulse instability in the plasma, resulting in a superior level of precision in the measurement. Reference atomic emission line intensity information from the Kurucz's spectral line database was used to perform spectral fitting.[18] The areas under selected spectral peaks, at target wavelengths, were used to quantify elemental concentrations. The overall time for sample processing, including sample and chamber preparation, LIBS processing, and data archiving was on the order of 15 min per sample.

Calibration of the LIBS data for elemental composition determination was performed comparing "like with like." This comparison consisted of matching up LIBS intensity measurement-derived concentration of individual elements with the concentration of oxides of the same element provided from standardized laboratory analysis. Calibration is the most difficult issue in LIBS data processing, especially for field measurements. In addition to the variables related to emission spectra, several other variables affect the intensity of the LIBS signal. These are: the fluctuation of incident laser energy; the size and density of particles and associated sample matrix; the location of the focus point; and the surface feature and history of ablation by laser shots. Samples of coals collected for the laboratory measurements were used as calibration standards. These samples covered an expanded range of analyte concentrations expected in the field demonstration. These calibration samples were characterized using standard ASTM measurements (ash composition). The LIBS system was used to measure the calibration samples. Linear calibration curves were constructed over the measured elemental concentration range. Subsequent samples were analyzed via direct comparison to the calibration curve parametrization. It should be noticed that the calibration curves establish a relationship between concentrations of oxide forms of elements, from calcinated samples of coal (or coal ash) analyzed with the standard procedure, while the LIBS-determined data is obtained from ablation of a coal sample and the spectral produced by all the elemental components in the sample. The calibration curves make it possible to relate both sets of data.

(17) Li, J. *Optics Laser Technol.* **2009**, *41*, 907–913.
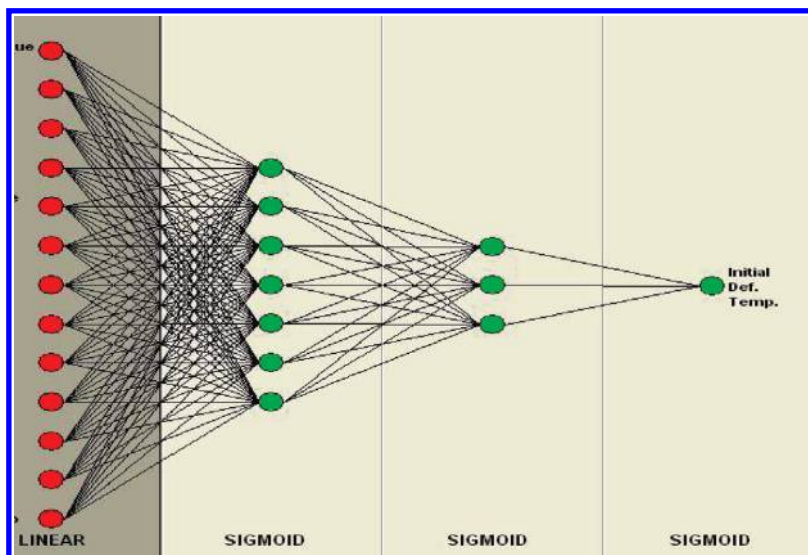(18) Atomic Spectral Line Database Built from atomic data files from R.L. Kurucz' CD-ROM 23. URI: http://www.pmp.uni-hannover.de/cgi-bin/ssi/test/kurucz/sekur.html, 2009.

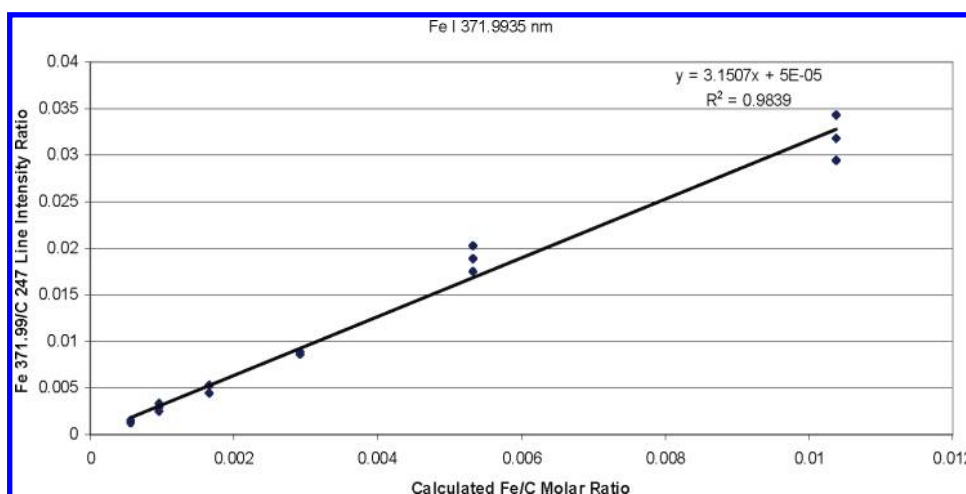**Figure 2.** ANN architecture for fusion temperature prediction.

Figure 3. Correlation for Fe emission line in synthetic coal.

Additionally, artificial neural network (ANN) models were used to relate the elemental composition measured by the LIBS system to the corresponding initial ash deformation temperature under reducing conditions. In recent years, ANNs has been proven very useful in the analysis of complex and uncertain data (which is a common feature of the LIBS data). A neural network is a system of interconnected processing elements, inspired by the network structure of the brain, which learns (training) the relationship between input data vectors and the output(s). The NeuFrame v.4 software package from Neusciences, UK, was used to establish functional relationships (nonlinear mapping functions) between LIBS-based coal elemental information and ash initial deformation temperature. The elements of interest (Al, Ca, K, Mg, Na, Fe, Si, and Ti) were configured into 13 input parameters (individually or in combination). The following parameters were used in the formulation, silica value, base, acid, R250 (relates slagging to the deposit's viscosity), dolomite ratio, and base/acid ratio, defined as: (1) silica value = Si/(Si + Fe + Ca + Mg); (2) base = Fe + Ca + Mg + K + Na; (3) acid = Si + Al + Ti; (4) R250 = (Si + Al)/(Si + Al + Fe + Ca); (5) dolomite ratio = (Ca + Mg)/(Fe + Ca + Mg + K + Na); (6) base/acid ratio = (Fe+ Ca + Mg+ K + Na)/(Si + Al + Ti).

It should be noticed that these parameters were defined in a similar fashion as the parameters used to characterize slagging; however, elemental (not oxide) concentrations derived from LIBS were used in their calculations.

The type of ANN used for this application was a feed-forward network with back-propagation learning. The transfer functions applied to each of the layers are included in Figure 2.

4. Results and Discussion

Figure 3 illustrates data obtained from the synthetic coal samples for iron. The elemental correlations between the measured LIBS intensity lines and the actual elemental molar ratio were referred to the 247 nm emission line corresponding to carbon. R^2 values were obtained for all the synthetic coal elemental correlations. The R^2 for the different elemental ratios for the simulated coals were greater than 0.98, indicating a good correspondence between the LIBS measurements and the elemental to carbon molar ratio of the synthetic samples.

Figures 4a and 4b show calibration curves for selected elemental ratios for coal samples from the coal bank, Al and K.
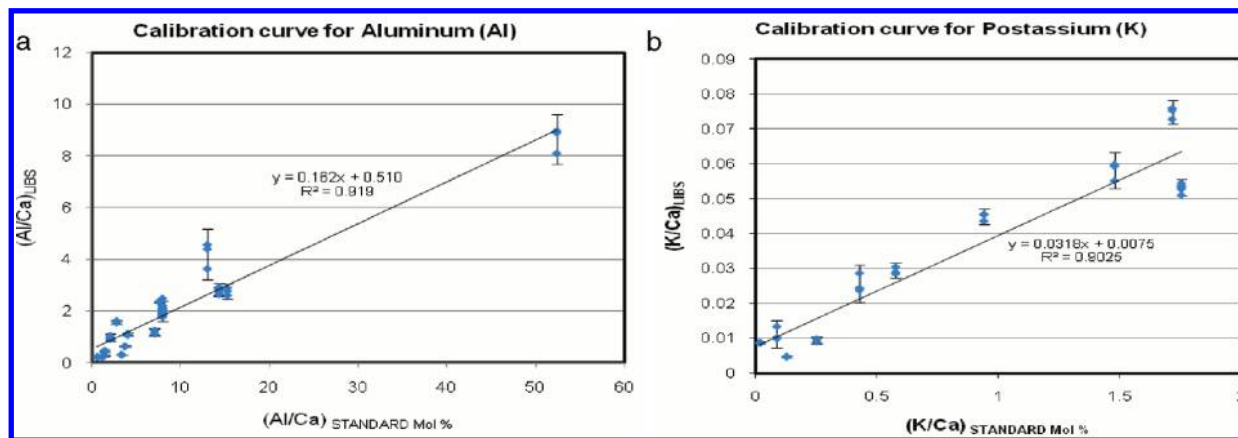
Figure 4. Calibration curves for (a) aluminum and (b) potassium.

Table 2. Results from Accuracy and Precision Tests

sample	wt % Mg	wt % Na	wt % K	wt % Fe	wt % Al	wt % Ca	wt % Si	wt % Ti
1	0.042	0.074	0.230	0.265	1.012	0.192	2.083	0.055
2	0.042	0.054	0.215	0.260	1.052	0.180	2.087	0.054
3	0.046	0.061	0.241	0.286	1.100	0.200	2.343	0.060
4	0.044	0.063	0.259	0.272	1.144	0.198	2.258	0.058
5	0.049	0.083	0.253	0.297	1.233	0.190	2.444	0.056
6	0.051	0.087	0.260	0.269	1.213	0.199	2.528	0.061
7	0.053	0.067	0.290	0.309	1.262	0.224	2.753	0.054
8	0.045	0.060	0.295	0.349	1.104	0.201	2.342	0.058
9	0.052	0.085	0.310	0.323	1.351	0.213	2.749	0.058
LIBS mean	0.047	0.070	0.261	0.292	1.163	0.200	2.398	0.057
stdev.	0.004	0.012	0.031	0.030	0.109	0.013	0.248	0.003

These curves were generated by plotting the measured LIBS intensity ratios versus the corresponding molar ratio estimated from the results from standardized chemical analyses. The LIBS measurements were setup in such way that a correlation between LIBS elemental intensity measurement and mole percentage of the oxides of the individual corresponding element is found from $x-y$ scatter plots. In these plots the *y*-axis is the count rate or emission intensity measured by the analyzer, and the *x*-axis is the elemental molar percentage directly measured by the standardized method (determined from ASTM laboratory results). When an unknown sample is measured, the measured intensity level for a particular element can be converted to a measured mass percentage by using the appropriate calibration equation for that element and molecular weight-based calculations. Selected individual elemental intensity values were normalized with respect to the matrix, by using the Ca emission line. This normalization was done to minimize the impact of the variability of the background emission level in each individual set of measurements. All of the calibration curves exhibited linear responses. No sign of spectral saturation was observed from the data, which may occur at high concentrations of a particular element, due to the ability of the atoms to absorb the emitted energy. The error bars shown in these figures represent two standard deviations of each data set for each coal and are the errors associated with the measurement at each particular concentration. The bold diagonal line in Figures 4a and 4b is a least-squares linear fit to the data that is used to determine the calibration equation. The calibration curves lead to good results, considering the broad range of concentrations for each elemental ratio, and the range of coals with dissimilar ranks. The R^2 of the correlations range from 0.814 for Mg to 0.993 for Fe.

The accuracy and reproducibility of the elemental measurements made with the LIBS system were ascertained from measurements on multiple samples of a particular Eastern US bituminous coal. Accuracy was defined as the deviation of the average LIBS measurement from the "true" value from the same sample, obtained by an independent analytical technique, in this case the ASTM standard. Reproducibility or measurement precision was defined as the percentage one standard deviation of the set of results represents from the average value. A total of nine individual runs were performed through the LIBS measurement cycle. Table 2 includes the results of this accuracy and precision test. The average measurement difference between the LIBS and standardized measurements was found to be better than 15% (absolute) for all elements, except for magnesium and potassium. The disparity for Mg and K could be attributed to the overlapping nature of the Mg spectral line with Fe and the performance of the photodiode for K detection. The repeatability tests indicate that for a 68.3% confidence limit the precision in the LIBS measurements is smaller than 18% for all the elements.

A laboratory-derived database was created for ANN training, based on the LIBS test results for all 16 coals in the coal bank. The inputs to the ANN model were configured using the set of LIBS-generated elemental intensities. The output for the ANN model was the ASTM initial deformation temperature at reducing conditions obtained from the ASTM results for the 16 coals. Network architecture selection was performed by trial-and-error, selecting a network with the minimal training error. This model was tested in the field at Brayton Point Station in the U. S., under static measurements conditions performed at the Brayton Point Station's chemical laboratory. The Brayton Point Station has three coal-fired units and one oil-fired unit, with an installed generating capacity of
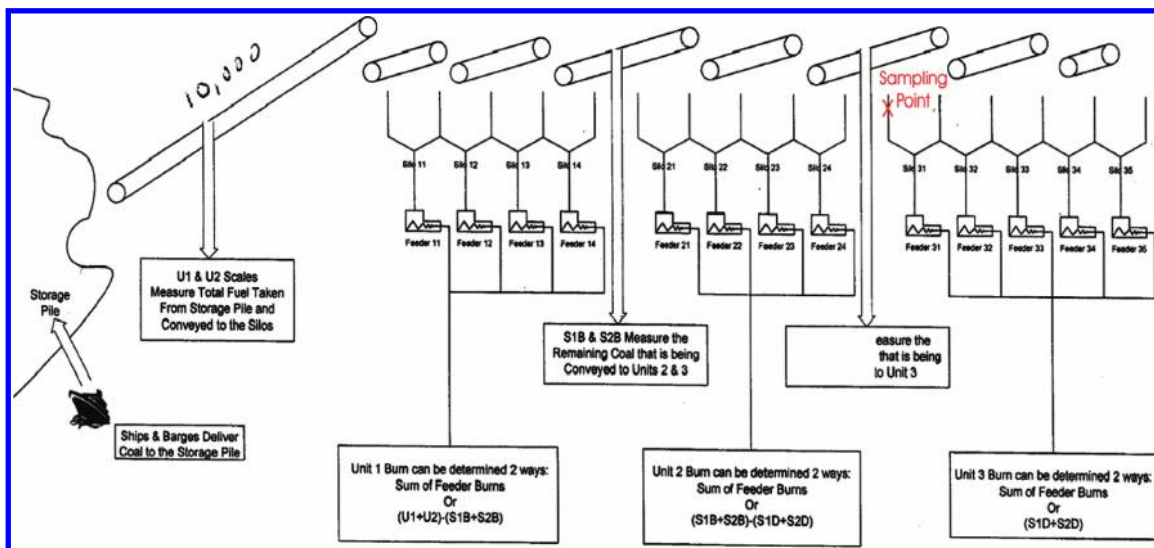
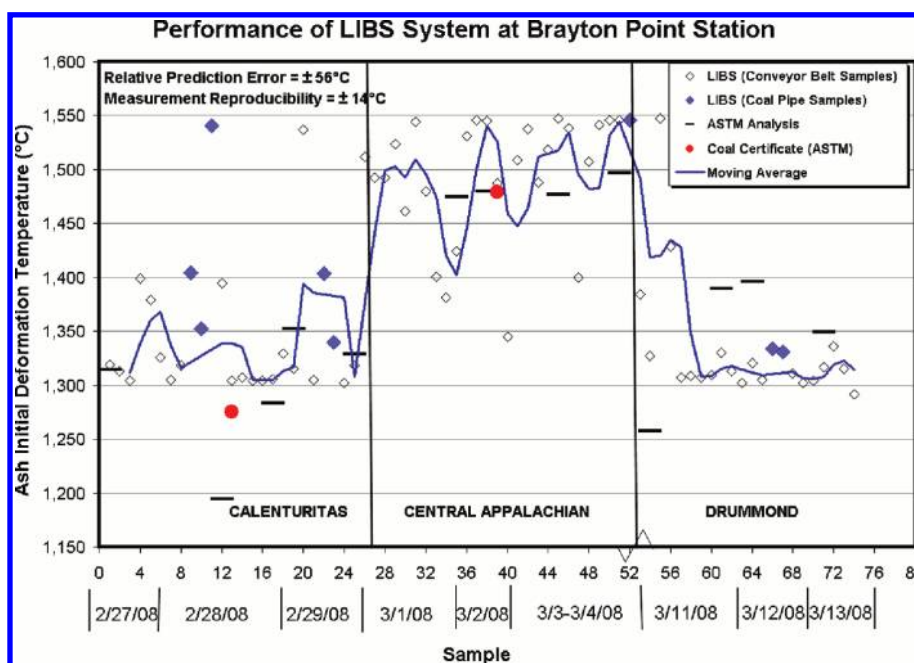**Figure 5.** Layout of coal delivery system at Brayton Point Station.

Figure 6. Comparison of predicted and measured fusion temperatures at Brayton Point Station.

1600 MW (1150 MW coal-fired). The station burns approximately 400 tons of coal per hour, when the coal-fired units operate at full load. The Brayton Point fuel feedstock is composed of Eastern US bituminous coals and a variety of South American coals from Colombia and Venezuela. The variability in coal feedstock at Brayton Point poses a significant challenge to the station. Some of the coals used at the station have a mineral composition that is susceptible to high-temperature slagging. Thus, at times, the station needs to take remedial actions on a retroactive basis, to mitigate the impact of slagging fuels. Brayton Point Station monitors furnace exit gas temperatures (FEGTs) with optical pyrometers, and fires the coal-fired boilers and activate boiler sootblowers to maintain a target FEGT level that does not exceed the fusion temperature of the ash.

Figure 5 shows a layout of the coal delivery system at Brayton Point. The majority of the samples collected for the

LIBS testing were grab samples obtained from the conveyor belt that supplies coal to the 31-feeder at Brayton Point Unit 3. These grab samples were crushed, sieved to a size smaller than 60 mesh, and dried to remove the superficial moisture, prior to be analyzed by the LIBS system. Additional coal samples were collected from coal pipes associated to the burners linked to the 31-pulverizer. The coals tested sequentially in the LIBS system field trail were Calenturitas (from Colombia), Central Appalachian, and Drummond (from Colombia), in that order. These coals are known for having a relatively low, high, and low fusion temperature, respectively. Splits from selected coal samples were sent out to an outside laboratory for ASTM analyses. Once the ASTM analyses of the coal samples were completed, those results were compared to the corresponding data from the analyzer.

Figure 6 shows a summary of the results obtained at Brayton Point, in terms of coal ash initial deformation

temperature. Figure 6 displays the LIBS-based results obtained from the ANN fusion temperature model and ASTM analyses for the three distinct coals, Calenturitas, Central Appalachian, and Drummond. The fusion temperatures reported with the certificates of coal quality provided by the station are also included in Figure 6. A total of 25, 27, and 22 conveyor belt and coal pipe samples were analyzed for each of the coals, respectively. The comparison between LIBS-based and ASTM fusion temperatures for Calenturitas, Central Appalachian, and Drummond coals is: 1334 vs 1294 °C, 1494 vs 1482 °C, and 1333 vs 1348 °C, respectively. Overall, there was no distinguishable difference between the fusion temperature levels obtained from samples collected from the conveyor belt and the samples collected from the coal pipes. Although, the mill pyrite rejection design should contribute to a change in coal elemental composition and fusion temperature, the sample preparation (grinding, sieving, and drying) used for the grab samples may have precluded noticing the differences between both sample sets.

To compare the results from both methods (LIBS and ASTM), an average relative prediction error was calculated to evaluate the prediction accuracy of the LIBS technique, according to $[\Sigma\,(T_{LIBS} - T_{ASTM})^2/N_{LIBS}]^{1/2}$. Where N_{LIBS} is the number of samples used in the comparison, and T_{LIBS} and T_{ASTM} are the fusion temperatures evaluated by both methods. The average relative fusion temperature prediction error for all three coals tested at Brayton Point is ±56 °C, which may be adequate for the use of LIBS in coal-fired power plants applications to detect changes in slagging propensity of coals, based on their fusion temperatures. The average prediction precision for the LIBS measurements performed at Brayton Point was calculated using the average relative standard deviation for the three coals, per $\Sigma\,2.57\sigma/N_{LIBS}^{1/2}$, for less than 1% error (confidence level of 99%). Where σ is the standard deviation obtained from all the predicted temperatures. The average precision for the LIBS measurements for all three coals is ±14 °C, which is a value that is within the tolerance on the measurement for repeatability and reproducibility of the ASTM method for ash fusion temperatures.

From these results, it is apparent that the lack of accuracy in the prediction of sample elemental concentration by LIBS can be compensated by the formulation of LIBS-based input parameters and the robustness of the ANN models for fusion temperature prediction. It should be noticed that the data from two of the fuels tested at Brayton Point, Calenturitas and Central Appalachia, did not participate in the AI model training. Furthermore, the rolling average trend in Figure 6

indicates that if LIBS analysis were performed with an online system on an hourly basis, the LIBS technology would be capable of providing predicted fusion temperature feedback with enough resolution to advise of changes in fuel quality that may affect the operation of coal-fired boilers sensitive to slagging impacts.

5. Conclusions

A LIBS system was developed and tested in the laboratory and at a power plant to demonstrate the feasibility of LIBS to measure coal ash composition, and a concept to predict coal slagging potential via fusion temperature neural network models based on LIBS emission intensity measurements. The optical setup consists of an excitation Nd:YAG laser, a sample chamber, optical spectrometer, a photodiode/amplifier unit, and a processing computer. The following elements were measured: Al, Ca, Mg, Na, Fe, Si, K, and Ti. LIBS measurement results were compared to independent ash minerals and fusion temperature measurements using ASTM Methods D6349 and D1857, respectively. It was found that the LIBS technology can yield sufficient accuracy and repeatability for commercial applications of LIBS for slagging monitoring. Static LIBS measurements performed at a coal-fired power plant with three different coals indicate an average relative fusion temperature prediction error for all three tested coals of ±56 °C, which may be adequate for the use of LIBS in coal-fired power plants applications, to detect changes in slagging propensity of coals based on their fusion temperatures. The average precision for the LIBS measurements for all three coals is ±14 °C, which is a value that is within the tolerance on the measurement for repeatability and reproducibility of the ASTM methods for ash fusion temperatures. The results of this study indicate that this concept could be incorporated into an online design for real-time coal characterization. Work being carried out by the authors of this paper is concentrating on installing a LIBS system to operate continuously on flowing coal on a conveyor belt. Details being studied at the present include the exclusion of sample preparation and the design of the optics that incorporate a flexible focal distance and a novel focusing lens purging system.