

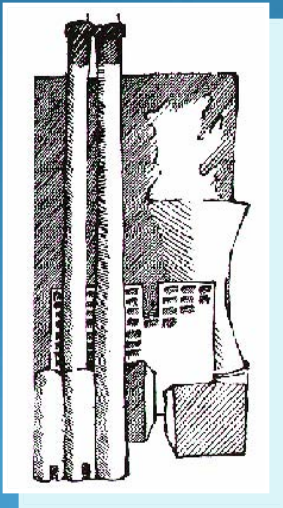
Reinhold Environmental Ltd.



2009 NO_x-Combustion Round
Table & Expo Presentation

February 9 & 10, 2009, Cleveland, OH

COAL CHARACTERIZATION AND SLAGGING CONTROL USING LASER BREAKDOWN SPECTROSCOPY ANALYSIS



*2009 NO_x Combustion – PCUG Conference
Cleveland, OH February 10, 2009*

Lehigh University

Carlos Romero
John Sale
James Yao

ERCo

Bob DeSaro
Joe Capraro
Ariel Weisberg
Samuel Lam



ERCo

ENERGY RESEARCH COMPANY

Lehigh University Energy Research Center

- More than 30 years of experience in the power industry
- Has active research programs in:
 - NO_x emissions control (developed Boiler OP).
 - Mercury emissions control (laboratory- and full-scale)
 - Slagging/Fouling and sootblowing studies (developed IntelliCLEAN).
 - Performance improvement (developed HEATRT, coal drying)
 - Materials, welding and catalyst development.
- Partnerships with utility companies, process providers, OEMs and others.

Energy Research Company

- **Energy Research Company (ERCo)** was formed in 1991.
 - ERCo is a small high-tech company that conducts research in industrial energy and emissions related areas.
 - ERCo is an OEM for Laser System for the Aluminum and Glass Industry.
 - ERCo has a number of federal and state R&D technology contracts as well as funding from commercial sources.
 - ERCo develops technologies that it owns and typically licenses to others for commercial deployment.
 - ERCo is at the Forefront of the Laser Induced Breakdown Spectroscopy (LIBS) Technology.

More information about ERCo can be found at:

www.er-co.com



Agenda

- Slagging and Fouling
- Cost and Energy Impacts
- Traditional Analytical Methods
- What is LIBS?
- LIBS Laboratory Experiments with Coal
- Brayton Point Field Tests
- DOE STTR Phase 1 Project
- LOFA System
- Future Work

SLAGGING AND FOULING

Introduction

- Fireside ash deposition is a major cause of downtime (derates and outages), and results in increased operation and maintenance costs for coal-fired power plants.
- The severity of the problem is related to the fuel characteristics, boiler design and operating conditions.
- The ash-forming constituents (**inorganics**) produce:
 - Accelerated rates of deposition on heat transfer surfaces.
 - Erosion and corrosion of boiler tubes.
 - Plugging of APHs and SCRs.
 - Difficult-to-collect particulate matter.
- The primary problem is when coal quality varies dramatically.
- Standardized analysis methods are too slow to be used effectively for fuel switching/blending and effective changes in plant operation.

Cost Impacts of Slagging and Fouling

- Cost due to slagging and fouling for a single power plant could be up to \$16 million per year.
- Energy losses of 268 trillion Btu/year throughout the US.
- Losses in revenue due to ash-related problems are estimated to be greater than \$2.4 billion/year for all U.S. coal-fired power plants.

Typical Slagging and Fouling



Superheater Slagging



Air Preheater Fouling

Boiler Slagging and Fouling

- Typically occurs in furnace section of a boiler (*burner belt, upper waterwalls and pendant surfaces*).
 - Deposits generally result from molten ash:
 - Molten ash impacts and sticks to tube surfaces.
 - Low-melting layer forms on deposits and captures fly ash.
 - Several mineral constituents in coals have been identified as “bad-actors” with respect to slagging.
- **Upper Furnace Waterwalls:** Buildup often occurs from fine clays containing **potassium** (*anthracites, foreign coals*).
 - **Burner Belt Region, Pendant Surfaces:** Slagging caused by **coarse pyrite** (FeS_2) for Eastern U.S. bituminous coals.
 - **Pendant Surfaces:** Common problem with blends of PRB/Bituminous coals due to **iron** and **calcium** compounds.



Major Slagging Mechanism en Bituminous Coals

- Pyrite Reactions:
 - $\text{FeS}_2 \rightarrow \text{FeS} + \text{SO}_2$
 - $\text{FeS} + \text{O}_2 \rightarrow \text{FeS/FeO}$ (MP = 1,700°F)
 - $\text{FeS} + \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3$ (MP = 2,850°F)
 - $\text{FeO} + \text{SiO}_2$ (quartz) $\rightarrow \text{FeSiO}_3$ (MP = 2,095°F)
- Incomplete oxidation favors formation of low-melting iron compounds:
 - Coarse pyrite
 - Reducing conditions
 - Pyrite encapsulated in unburned coal particles

Samples of Coal Composition

- The Glencore coal has higher moisture than the typical Central Appalachian coals (USGS Coal Quality Database – West Virginia, Kanawha County: 2-4% moisture)

| Summary of Coal Ash Indices | | | |
|------------------------------------|---------------|---|---------------|
| March 9, 2007 | | | |
| COAL SOURCE/BLEND | GLENCORE LTD. | EXPORTING COMMODITIES INTERNATIONAL | GLENCORE LTD. |
| COUNTY | SOUTH AMERICA | SOUTH AMERICA | COLUMBIAN |
| DATE ANALYZED | 1/23/2007 | 1/30/2007 | 3/6/2007 |
| SHIPMENT ID | 10107 | 20207 | 4987-1 |
| PROXIMATE ANALYSIS (% AS RECEIVED) | | | |
| TOTAL MOISTURE | 11.83% | 5.71% | 11.71% |
| RESIDUAL MOISTURE, % DRY | | | |
| ASH | 11.83% | 7.83% | 7.27% |
| ASH, % DRY | 13.42% | 8.30% | 8.23% |
| VOLATILE MATTER | 35.27% | 34.44% | 35.70% |
| VOLATILE MATTER, % DRY | 40.00% | 36.53% | 40.43% |
| SULFUR | 0.49% | 0.73% | 0.43% |
| SULFUR, % DRY | 0.56% | 0.77% | 0.49% |
| FIXED CARBON | 41.07% | 52.02% | 45.32% |
| FIXED CARBON, % DRY | 46.58% | 55.17% | 51.33% |
| TOTAL, % AS RECEIVED | 100.00% | 100.00% | 100.00% |
| TOTAL, % DRY | 100.00% | 100.00% | 100.00% |
| GROSS CALORIFIC VALUE, BTU/LB | 11,338 | 12,813 | 11,309 |
| LB SO ₂ /MMBTU | | | 0.3802 |
| LB ASH/MMBTU | 10.43 | 6.11 | 6.43 |
| HARDGROVE GRINDABILITY INDEX | | | 48 |
| ULTIMATE ANALYSIS (% AS RECEIVED) | | | |
| MOISTURE | | | |
| CARBON | | | 72.41% |
| HYDROGEN | | | 5.03% |
| NITROGEN | | | 1.44% |
| ASH | | | 8.23% |
| SULFUR | | | 0.49% |
| CHLORINE | | | 0.03% |
| OXYGEN | | | 12.37% |
| TOTAL | 0.00% | 0.00% | 100.00% |

Ash Mineral Analysis

- The Glencore coal has a reducing initial deformation temperature (IDT) of 2,462°F.
- This is lower than the IDT for typical Central Appalachian coals (USGS Coal Quality Database – West Virginia, Kanawha County: 2,700-2,900°F).
- Since the IDT can change up to 200°F with fuel changes or a surge of problem coal in a shipment, the ERC recommends the installation of Furnace Exit Gas Temperature (FEGT) probes.

| COAL SOURCE/BLEND | GLENCORE LTD. | EXPORTING COMMODITIES INTERNATIONAL | GLENCORE LTD. |
|---|---------------|---|----------------|
| ASH COMPOSITION (%) | | | |
| SILICA, SiO ₂ | | | 60.13% |
| ALUMINA, Al ₂ O ₃ | | | 19.85% |
| TITANIA, TiO ₂ | | | 1.07% |
| FERRIC OXIDE, Fe ₂ O ₃ | | | 7.74% |
| LIME, CaO | | | 2.13% |
| MAGNESIA, MgO | | | 1.64% |
| SODIUM OXIDE, Na ₂ O | | | 0.58% |
| POTASSIUM OXIDE, K ₂ O | | | 1.59% |
| MANGANESE OXIDE, Mn ₃ O ₄ | | | 0.00% |
| PHOSPHORUS PENTOXIDE, P ₂ O ₅ | | | 0.24% |
| SULFUR TRIOXIDE, SO ₃ | | | 3.37% |
| UNDETERMINED | | | 1.66% |
| TOTAL | 0.0% | 0.0% | 100.00% |
| PERCENT BASE | NC | NC | 14% |
| BASE/SODIUM RATIO | NC | NC | 24 |
| PERCENT ACID | NC | NC | 86% |
| ASH FUSIBILITY TEMPERATURES (DEG. F, REDUCING) | | | |
| INITIAL DEFORMATION TEMP, IT | | | 2,462 |
| SOFTENING TEMP, (H=W) ST | | | 2,551 |
| HEMISPHERICAL TEMP, (H=1/2 W), HT | | | 2,660 |
| FLUID TEMP, FT | | | 2,703 |
| FT-IT DIFFERENTIAL | 0 | 0 | 241 |

Slagging and Fouling Propensity

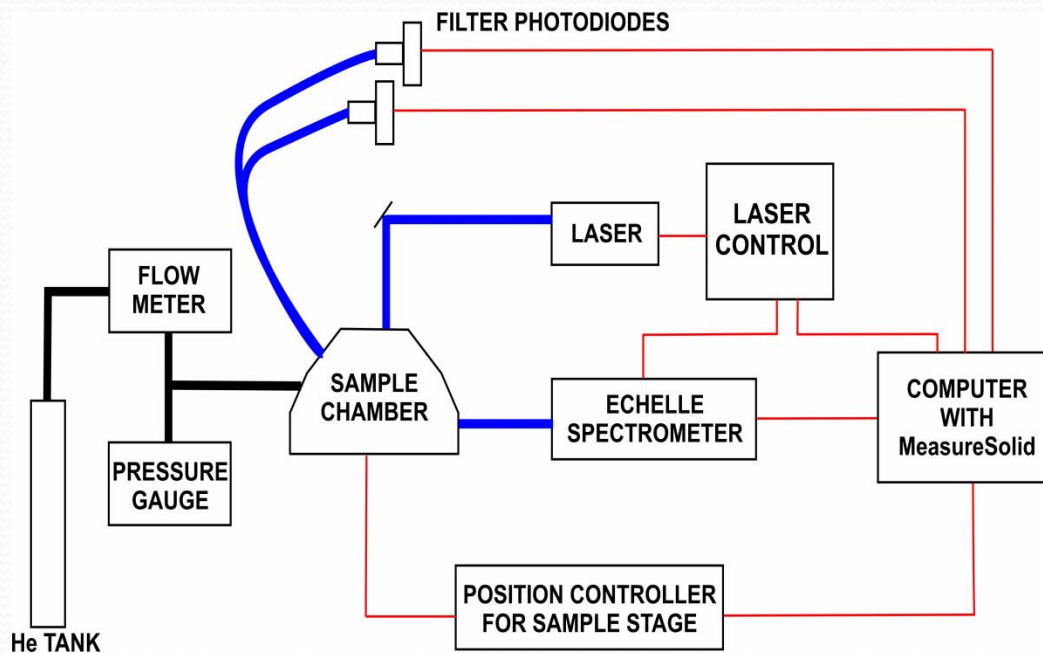
- The Glencore coal has a bituminous ash classification of 2.05.
- In general, the slagging and fouling indices of 0.17 and 0.10 are low, however:
 - the iron percentage, which increases the slagging potential, is medium
 - the silica/alumina ratio, which lowers the fusibility temperature and increases the slagging potential, is high and
 - the sodium content, which lowers the ash fusion temperature and raises the slagging potential, is medium
- These indicates that the coal may have a tendency toward slagging.

| ASH DESCRIPTOR | | | |
|--------------------------------|-----------|-----------|-------------------|
| DOLOMITE PERCENTAGE | NC | NC | 28% |
| IRON-OXIDE/DOLOMITE RATIO (AC) | NC | NC | 2.05 |
| ASH CLASSIFICATION (AC) | ND | ND | BITUMINOUS |

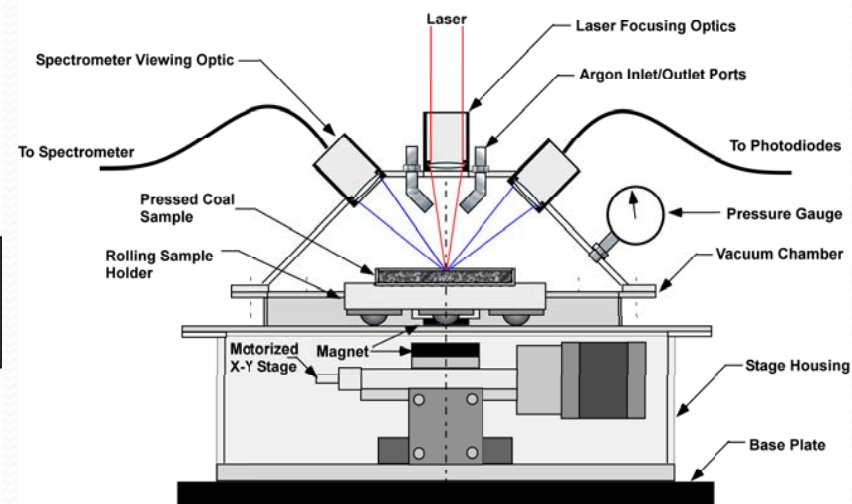
| SLAGGING PARAMETERS (NOTES 2, 3) | | | |
|---|------|------|--------------|
| BASE/ACID RATIO (NOTE 1) | NC | NC | 0.17 |
| SLAGGING INDEX-BITUMINOUS ASH (R _S) | NC | NC | 0.08 |
| INITIAL DEFORMATION TEMPERATURE (RED) | 0 | 0 | 2,462 |
| IRON PERCENTAGE | 0.0% | 0.0% | 7.7% |
| CALCIUM PERCENTAGE | 0.0% | 0.0% | 2.1% |
| IRON/CALCIUM RATIO | NC | NC | 3.63 |
| SILICA RATIO | 0.0% | 0.0% | 83.9% |
| SILICA/ALUMINA RATIO | NC | NC | 3.03 |
| (SILICA+ALUMINA)/IRON RATIO | NC | NC | 10.33 |
| (SILICA+ALUMINA)/CALCIUM RATIO | NC | NC | 37.55 |
| (SILICA+ALUMINA)/(IRON+CALCIUM) RATIO | NC | NC | 8.10 |
| (SILICA+ALUMINA)/(IRON+6*CALCIUM) RATIO | NC | NC | 3.90 |
| SLAGGING INDEX-VISCOSITY (R _{VS}) | NC | NC | NC |
| FOULING PARAMETERS (NOTES 4, 5) | | | |
| FOULING INDEX-BITUMINOUS ASH (R _F) | NC | NC | 0.10 |
| CHLORINE, % | 0.0% | 0.0% | 0.03% |
| SODIUM, % | 0.0% | 0.0% | 0.6% |
| TOTAL COAL ALKALI METAL CONTENT, % | 0.0% | 0.0% | 2.2% |
| EQUIVALENT SODIUM CONTENT | | | |
| SILICA/ALUMINA RATIO | NC | NC | 3.03 |
| SILICA/CALCIUM RATIO | NC | NC | 28.23 |
| (SILICA+ALUMINA)/CALCIUM RATIO | NC | NC | 37.55 |
| ASH VISCOSITY, °F | NC | NC | NC |

LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

LIBS Concept



LIBS Coal Analyzer Cut-Away View



LIBS Advantages

- Can be used *in situ*.
- Real-time feedstock measurements are possible.
- Works on both solids and liquids – dry pulverized coal, as well as coal slurries.
- Sensitive, accurate and high-repeatability.

LIBS Development

- Completed Work
 - Development of a LIBS measurement system.
 - Development of artificial intelligence-based correlations.
- Work In-Progress
 - Development of an on-line coal sampling system
 - Development of an on-line advisory software.
- Future Work – Field demonstration of the integrated on-line sampling, LIBS analysis and on-line advisory software system.

LIBS LABORATORY EXPERIMENTS



2009 NO_x-Combustion-PCUG Conference



ENERGY RESEARCH COMPANY 18

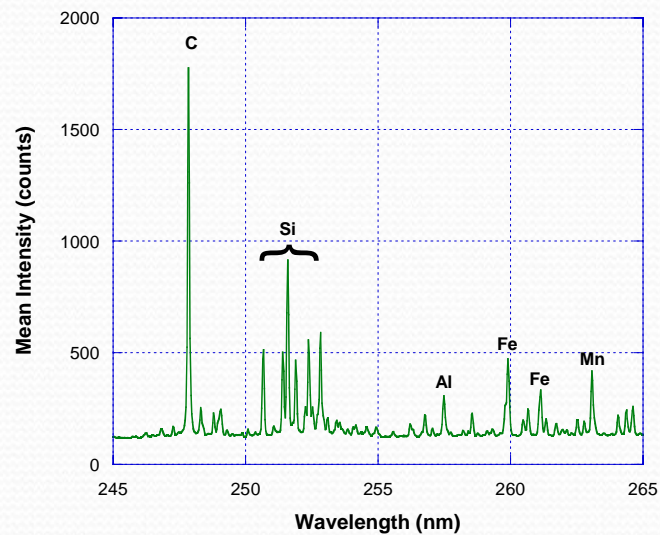
LIBS Laboratory Experiments

- Detection of elemental concentrations using synthetic samples.
- Detection of elemental composition from samples in a coal bank.
- Coal bank assembled with 16 bituminous and low-rank coals (11 bituminous ashes, 5 lignitic ashes).
- Initial deformation temperature range (under reducing environment) = 1,920 to 3,000°F.
- Sample preparation according to ASTM Method 2013.
- Experiments performed in 3 samples per coal, 60 shots per samples.

LIBS Coal Spectrum

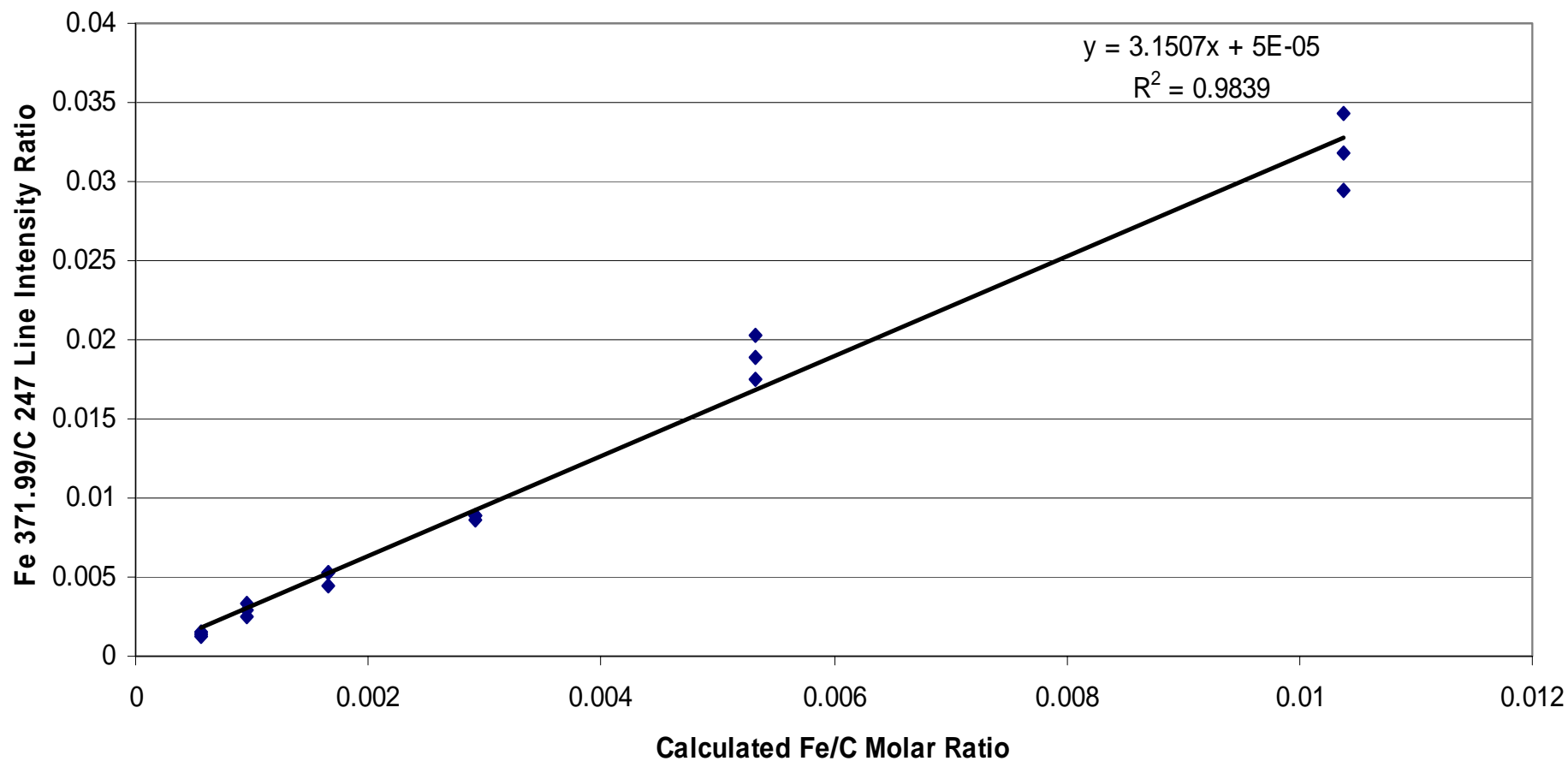
C = 75.13%
Si = 2.3%
Al = 1.6%
Fe = 1.1%
Mn = 77 ppm

$$I^{ji} = Fn \frac{A_{ji} g_j e^{-(E_j / kT)}}{Q(T)}$$

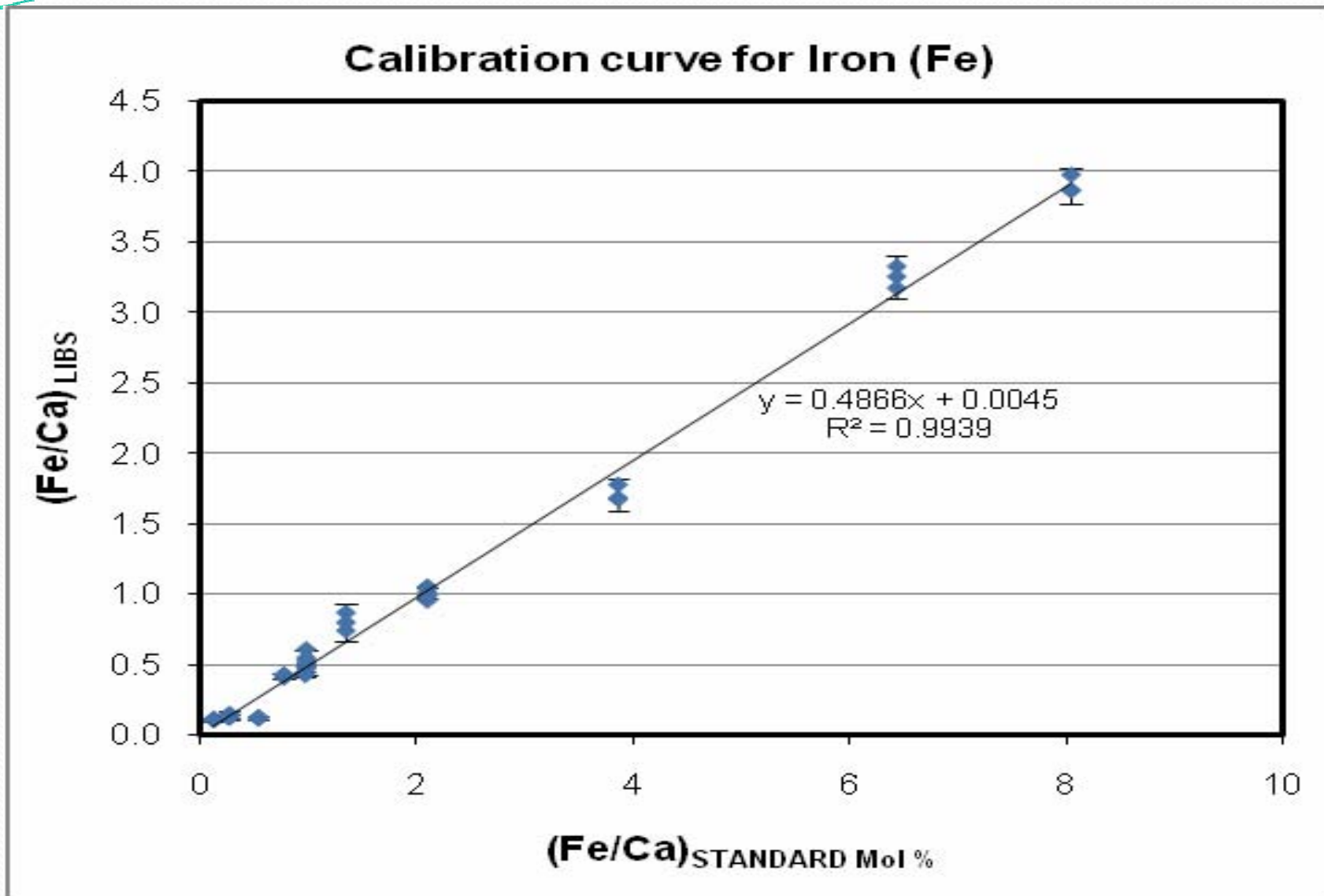


Simulated Coal Laboratory Results

Fe I 371.9935 nm



Coal Bank Laboratory Results



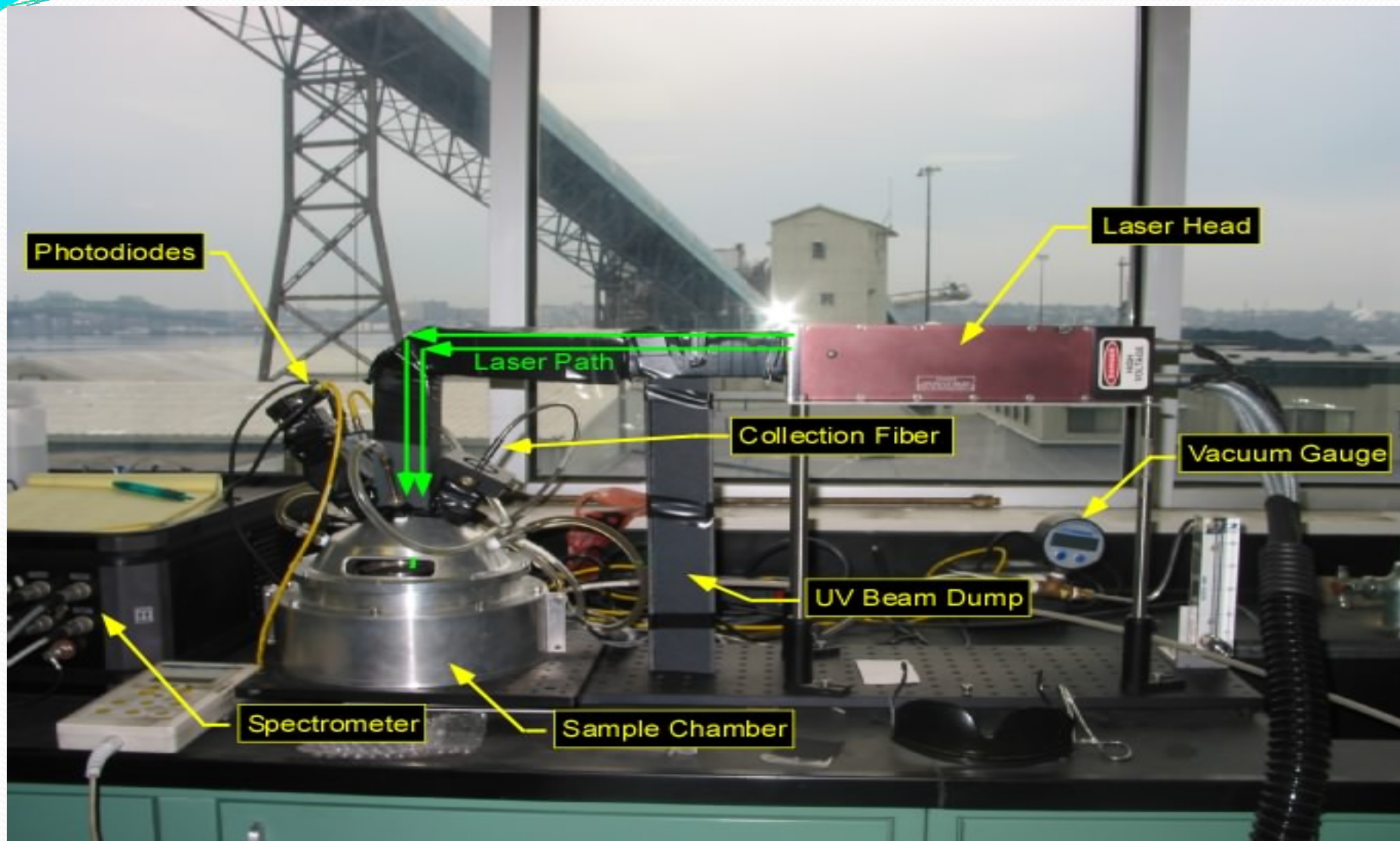
Coal Bank Laboratory Results

| 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 |
| SD | 0.004 | 0.012 | 0.031 | 0.030 | 0.109 | 0.013 | 0.248 | 0.003 |

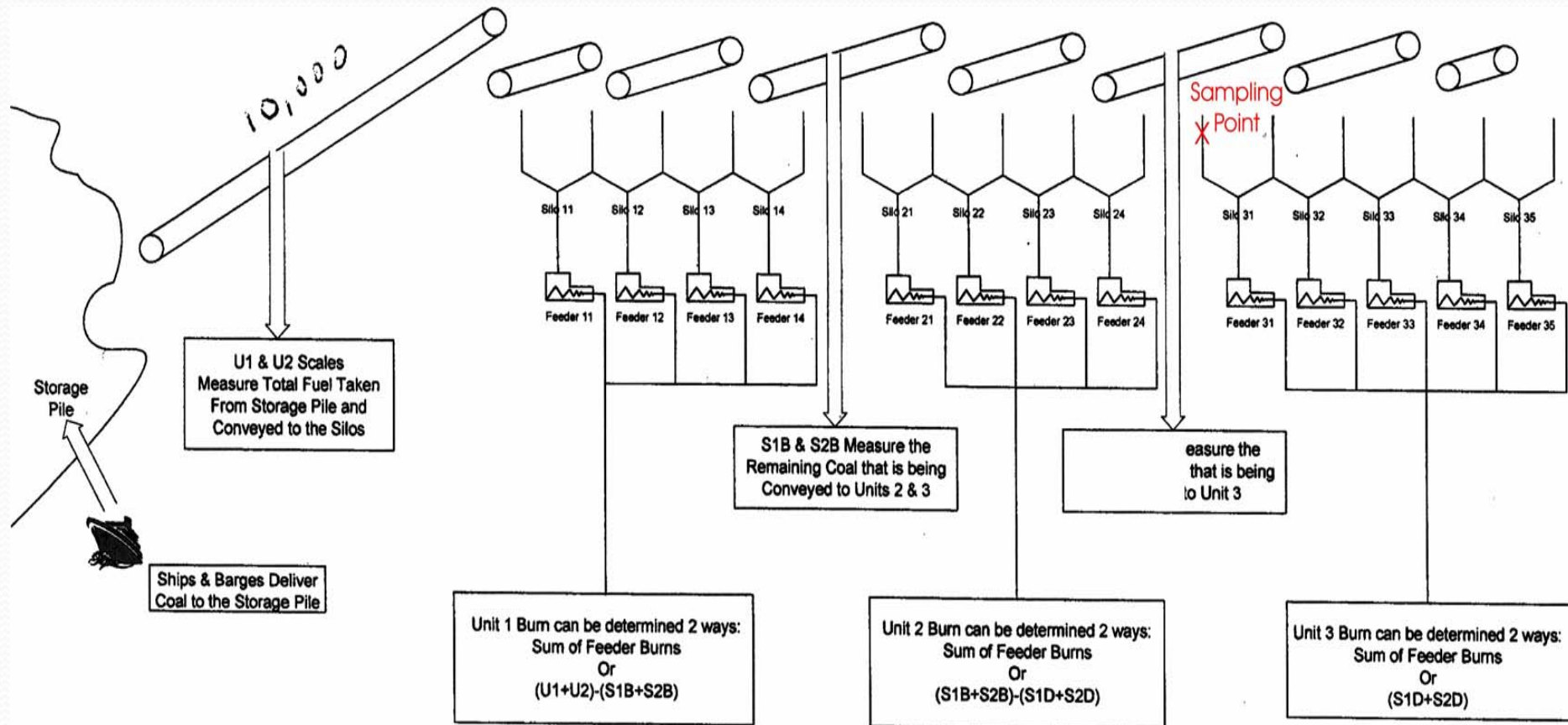


BRAYTON POINT FIELD TESTS

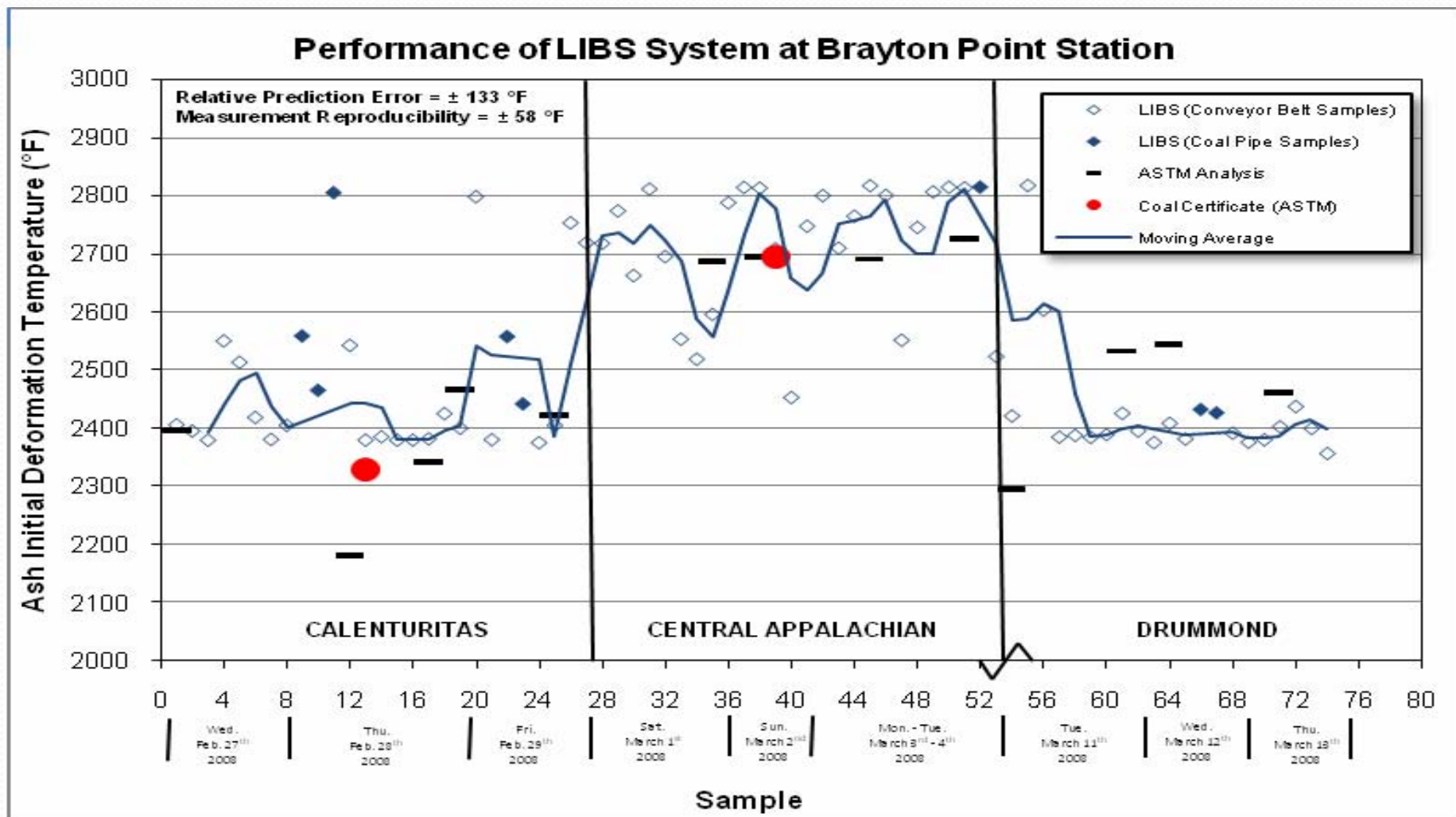
LIBS System at Brayton Point Station



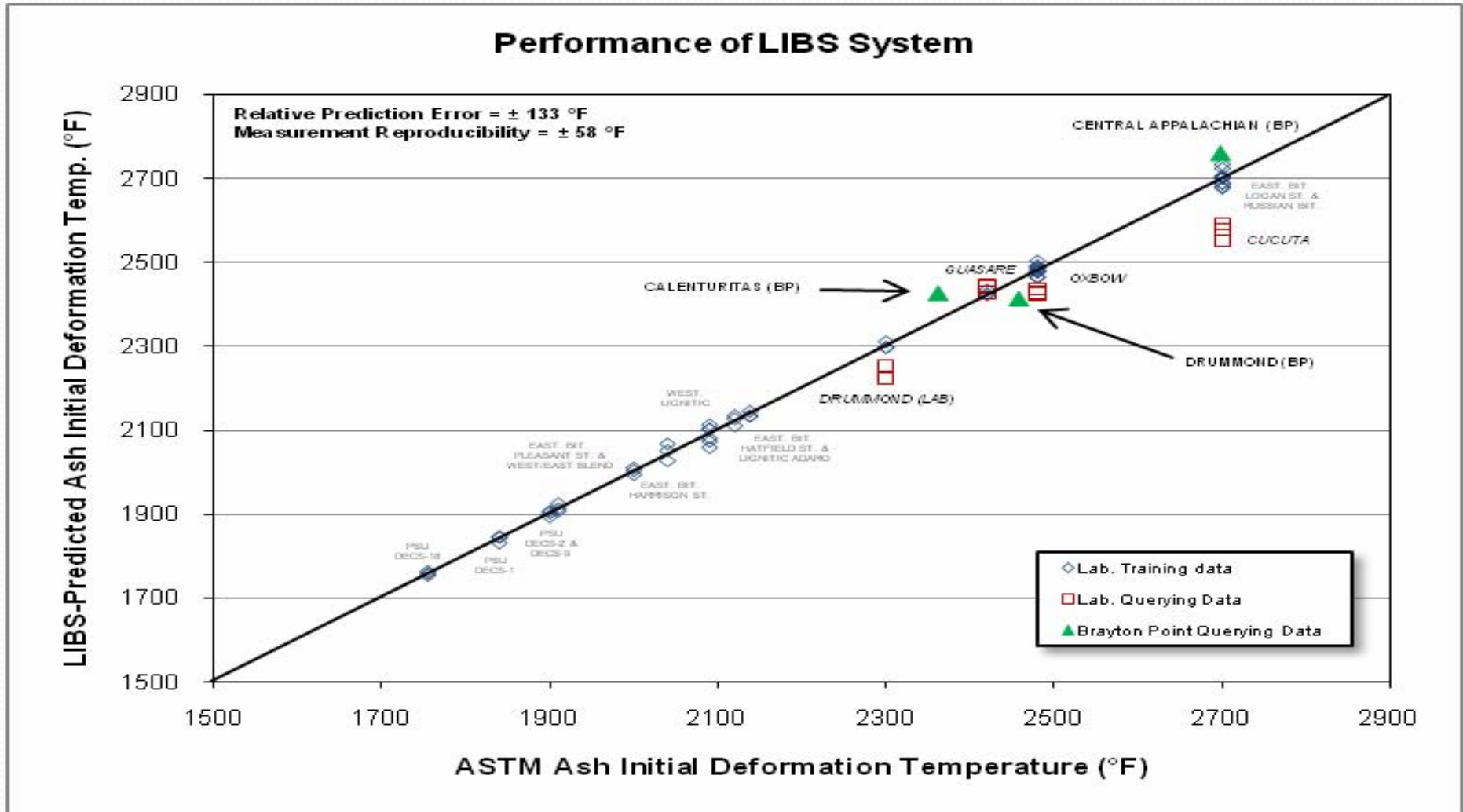
Field Testing at Brayton Point Station



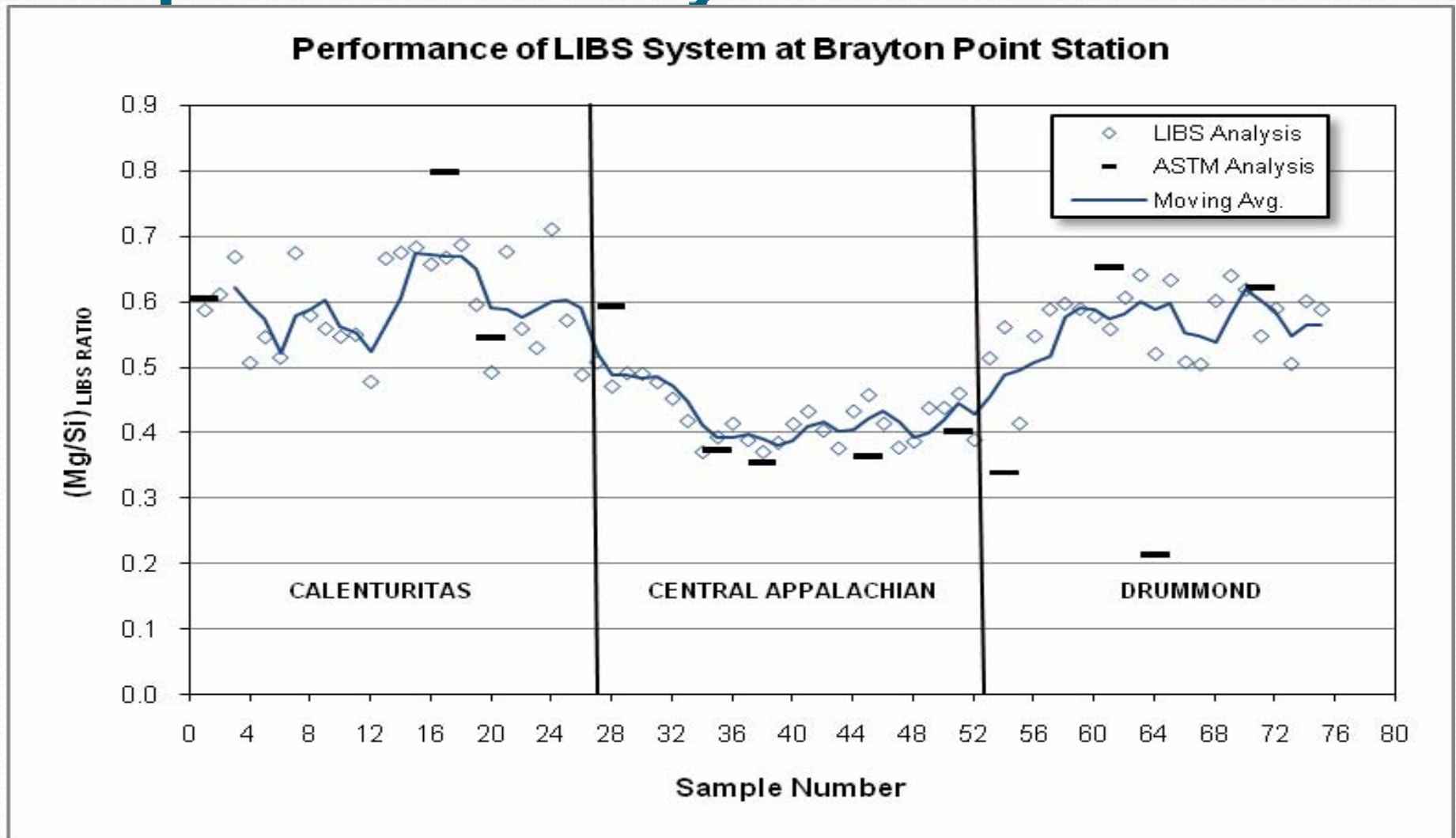
LIBS System Performance for T_f Prediction at Brayton Point



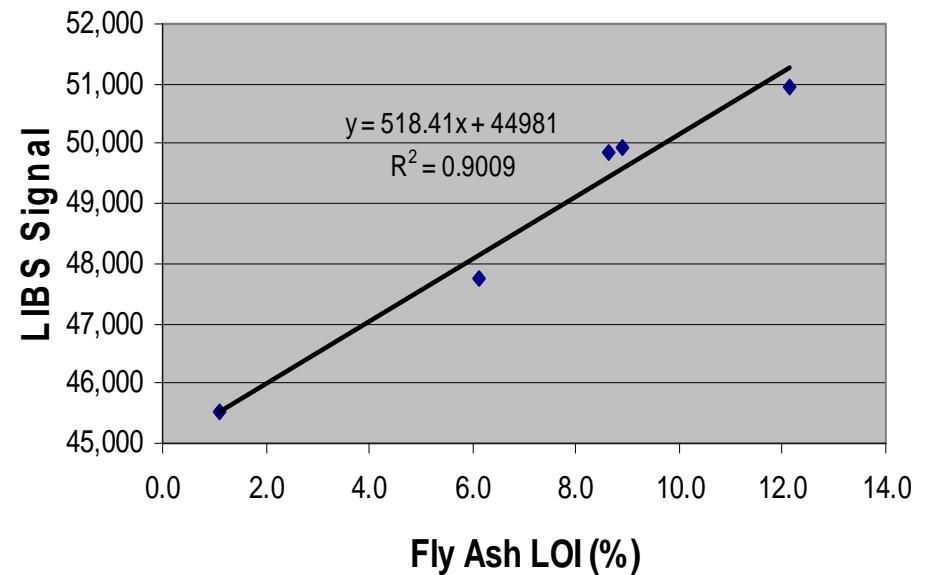
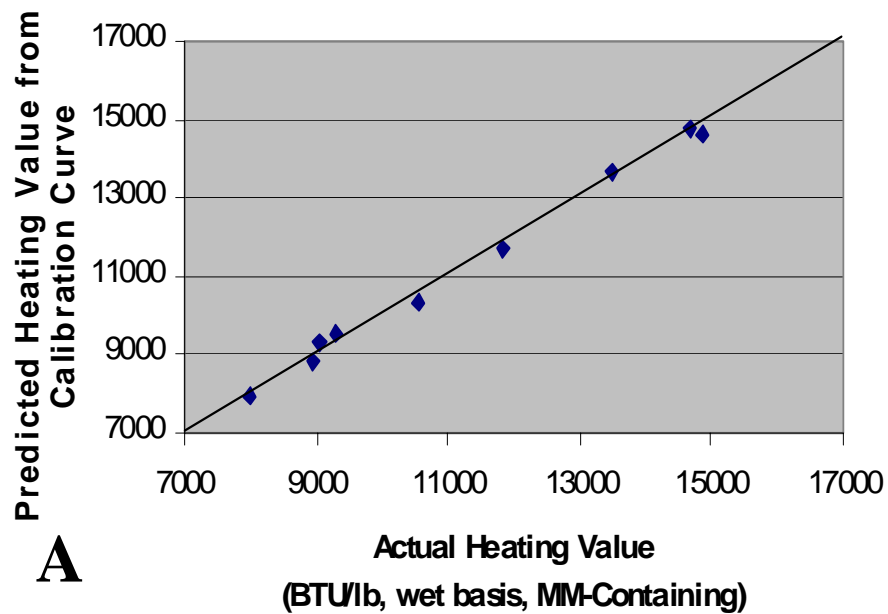
LIBS System Performance for T_f Prediction at Brayton Point



LIBS System Performance for Elemental Composition at Brayton Point



Additional LIBS Applications



DOE STTR PHASE I PROJECT

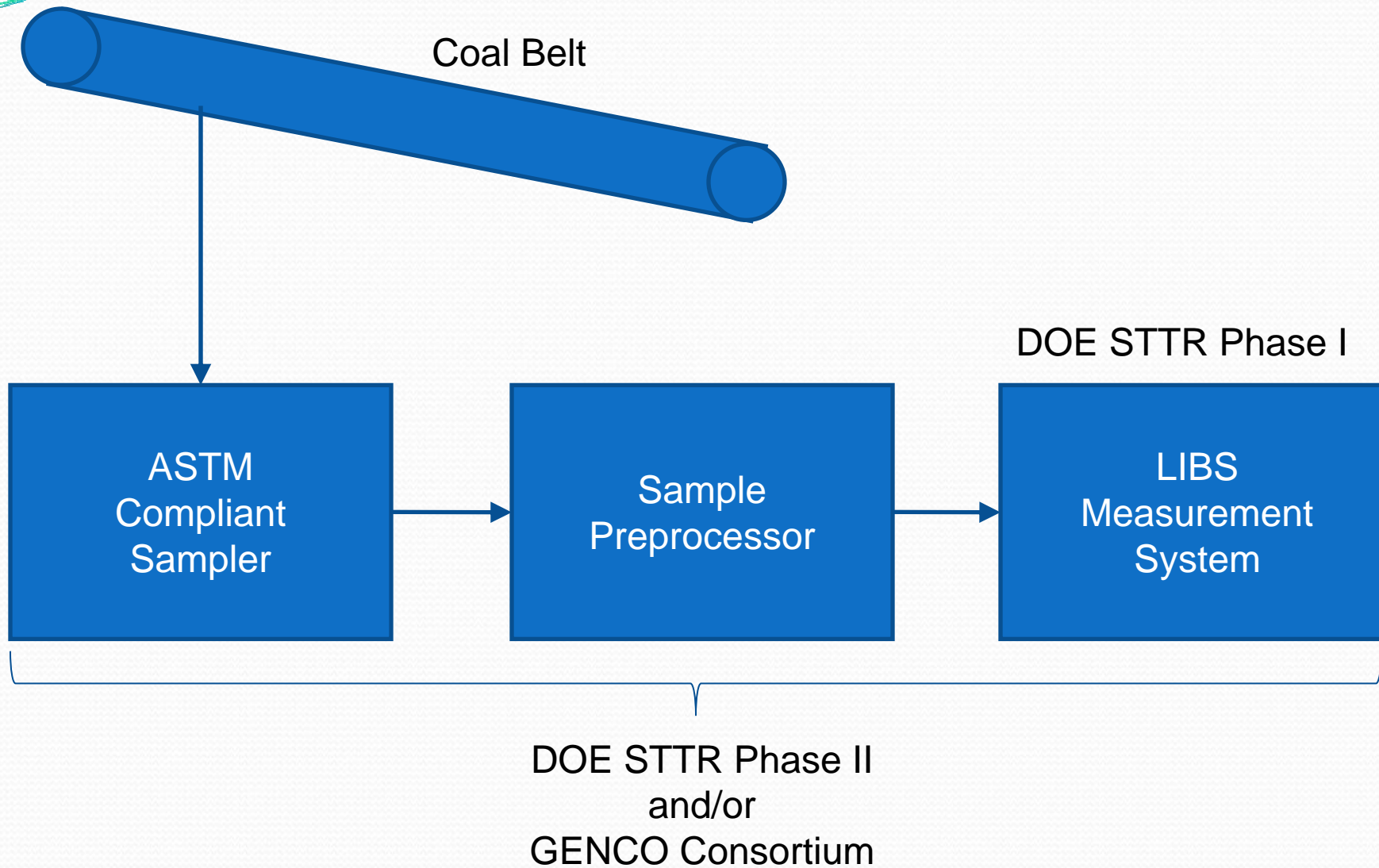


STTR Phase 1 Laboratory Work

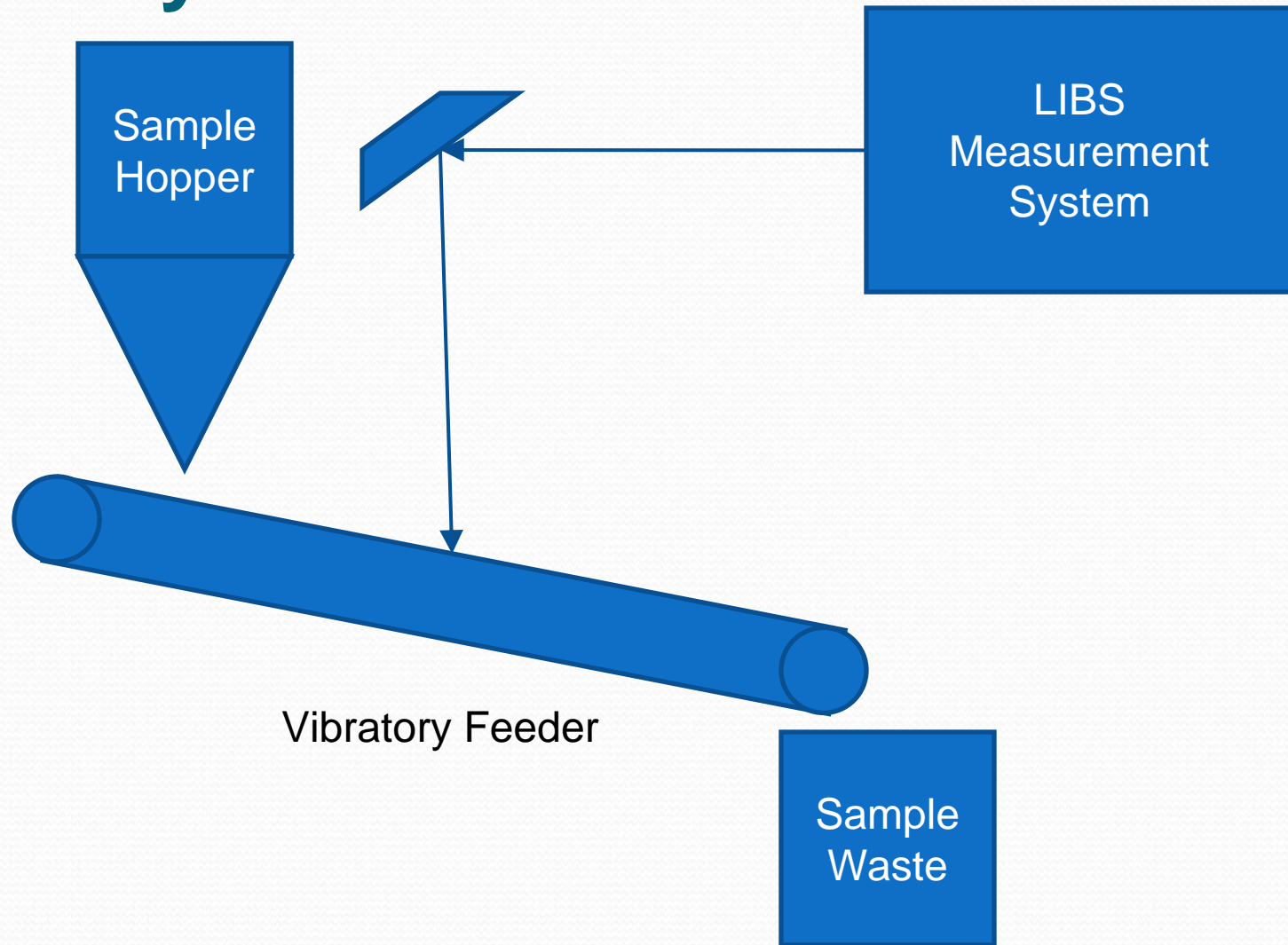
SIMPLIFY THE LIBS SYSTEM DESIGN

- Develop a new LIBS Prototype
- Integrate System Into a Coal Feeder System
- Conduct Laboratory Experiments to Optimize the LIBS Configuration
- Build a Field-Deployable LIBS Prototype (STTR Phase II)

LIBS Sampling System Development



LIBS Measurement System – Laboratory Simulation



Summary of System Improvements

- Can Work in Ambient Conditions:
 - No vacuum chamber needed
 - No gas purging system needed
- Amount of Equipment has been Reduced, Which Reduces System Weight and Cost.
- Laboratory Test Results Appears to be Comparable to the Brayton Point Field Tests.

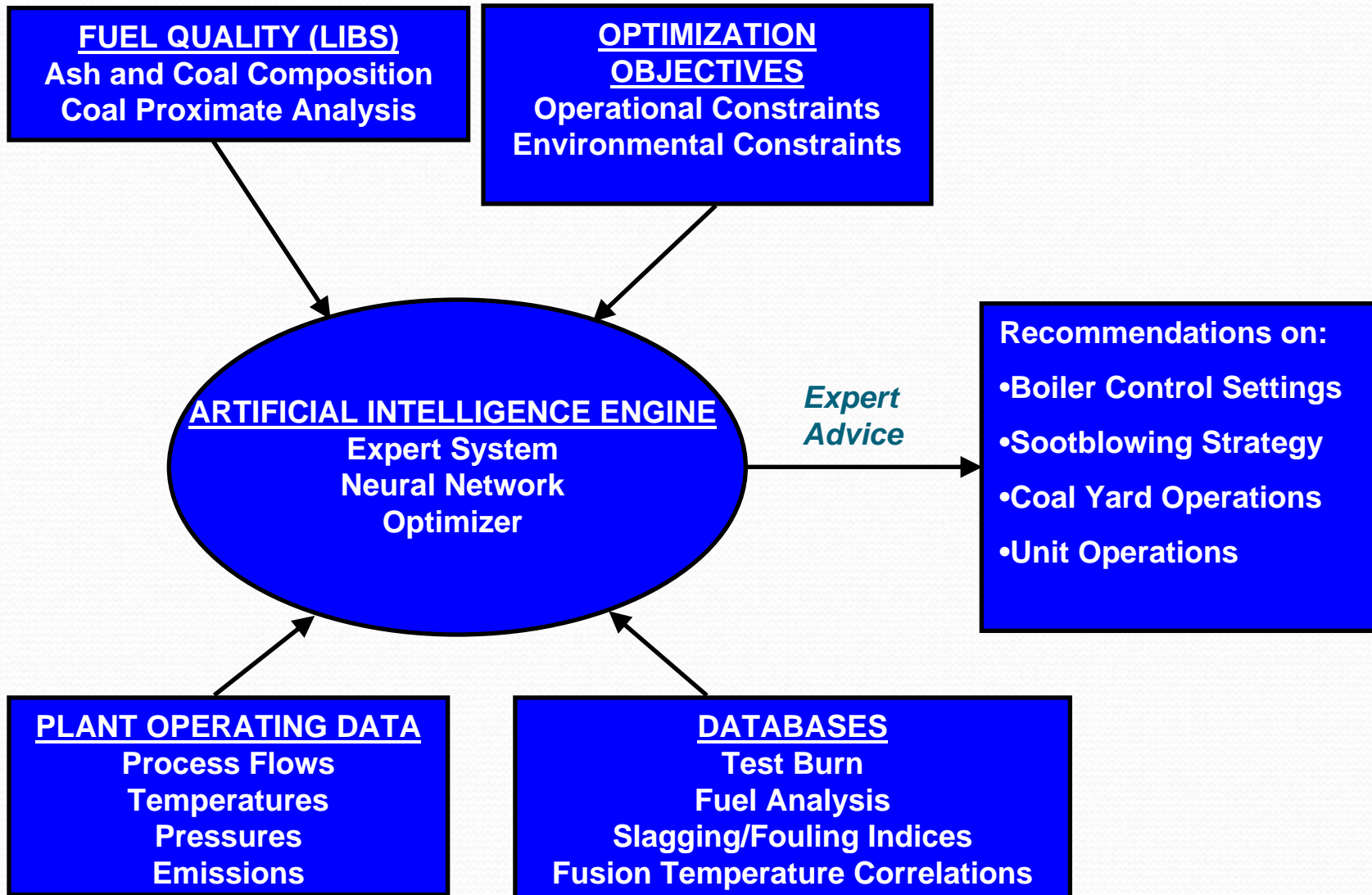
LASER ON-LINE FUEL ADVISORY (LOFA) SYSTEM

LOFA Concept

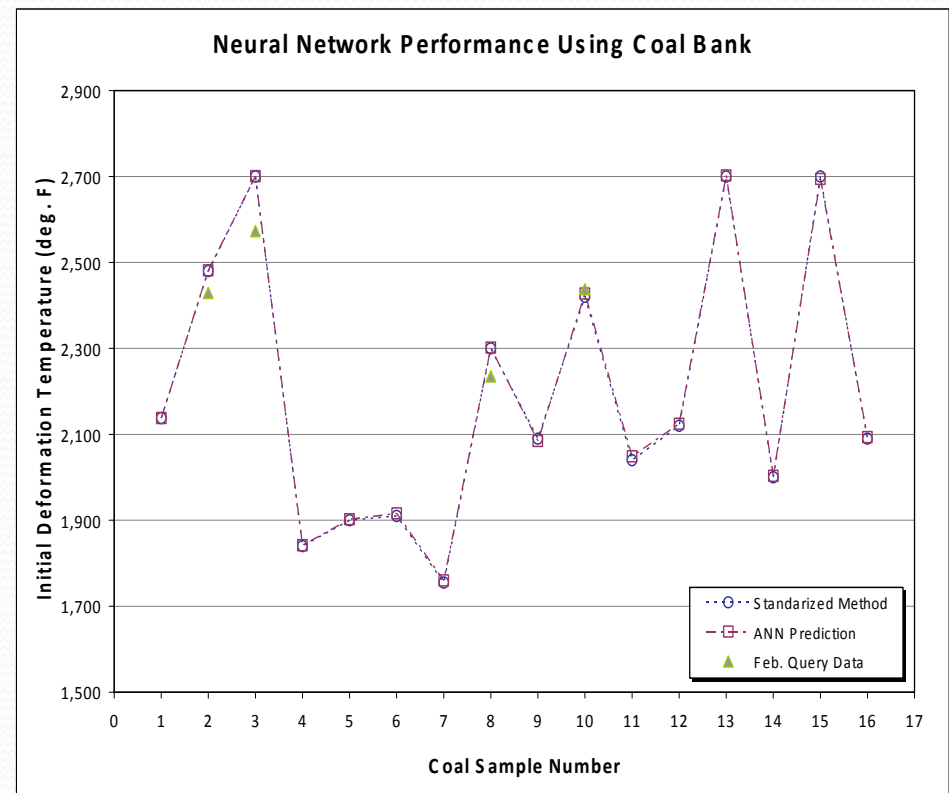
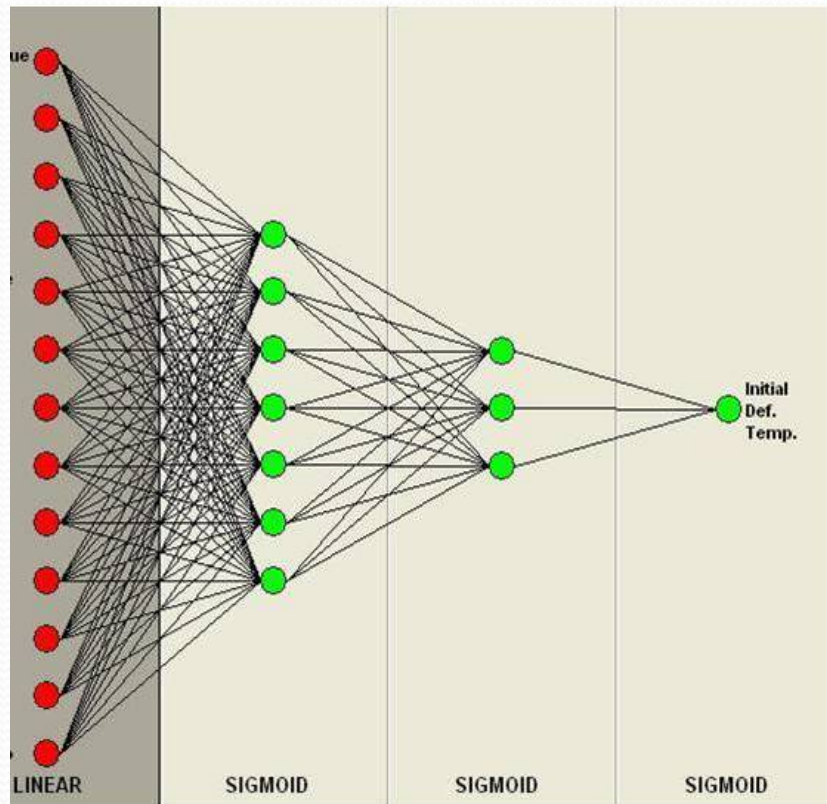
LASER ON-LINE FUEL ADVISORY (LOFA)

- LIBS is used to measure coal properties
- Other data from the plant is collected
- Artificial Intelligence (AI) techniques are used to process the data and provide advisory recommendations
- Plant operators adjust the boiler to mitigate slagging and fouling

LOFA Approach

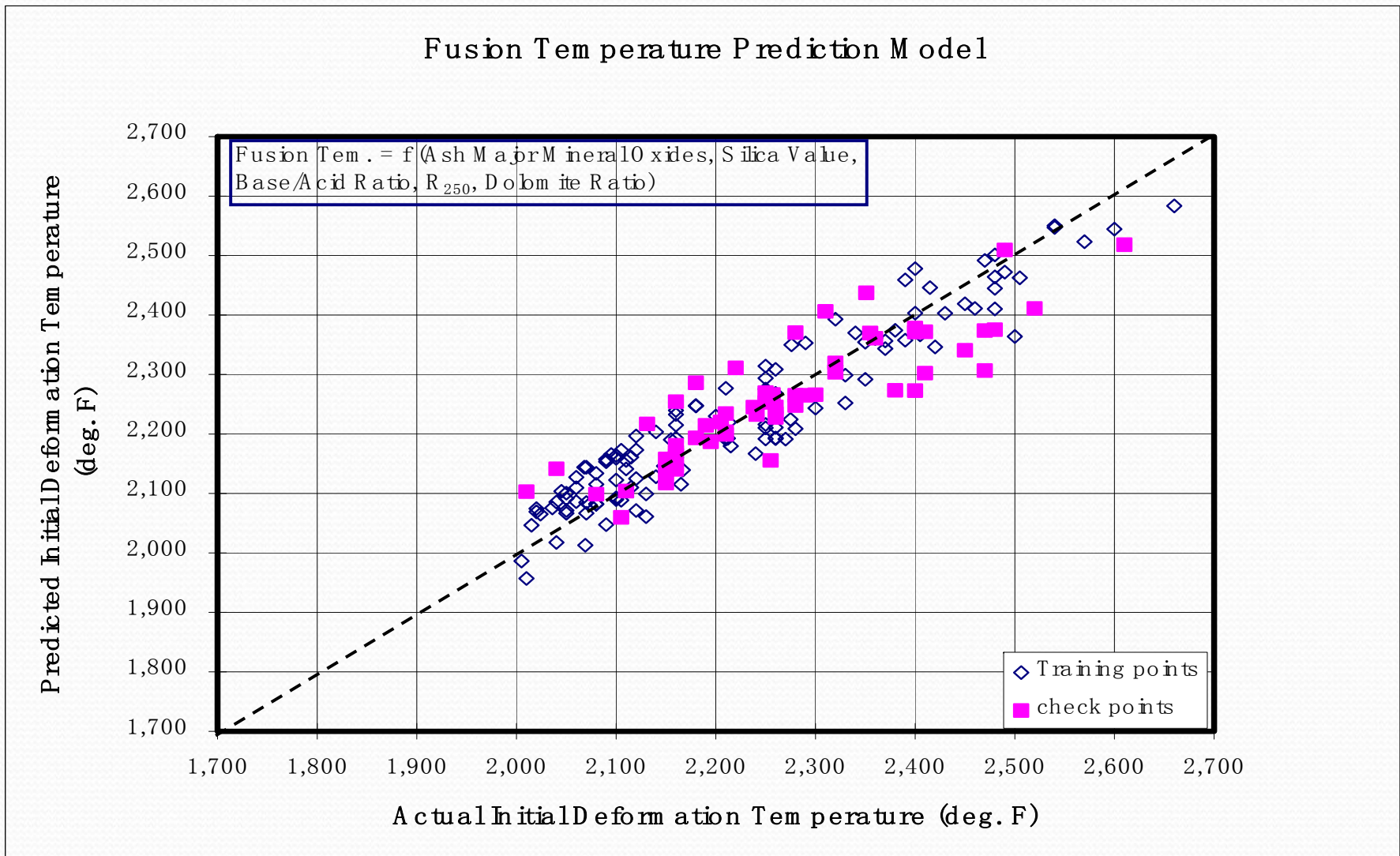


Neural Network Model Results



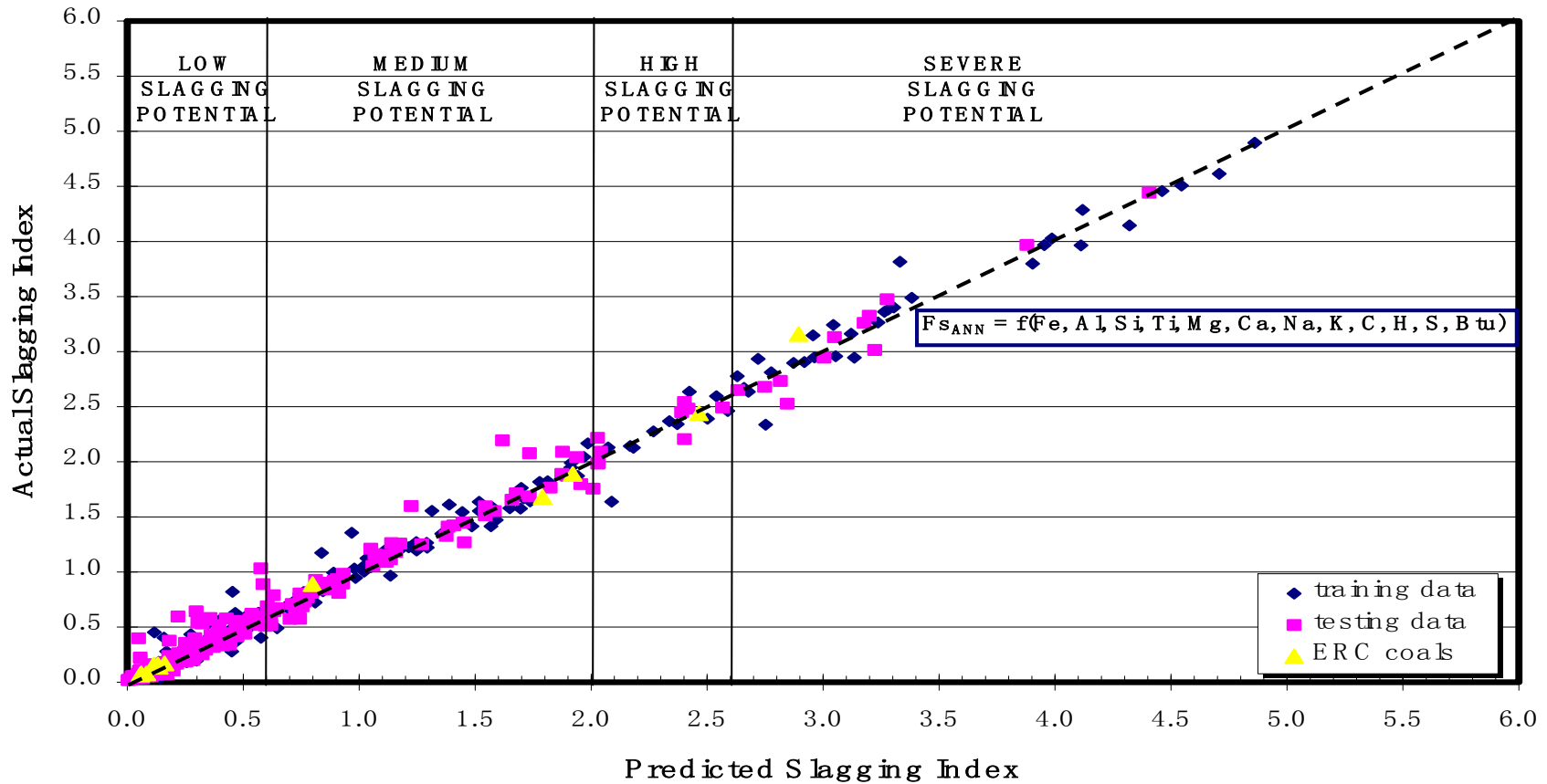
Artificial Neural Network Modeling

Fusion Temperature Prediction Model

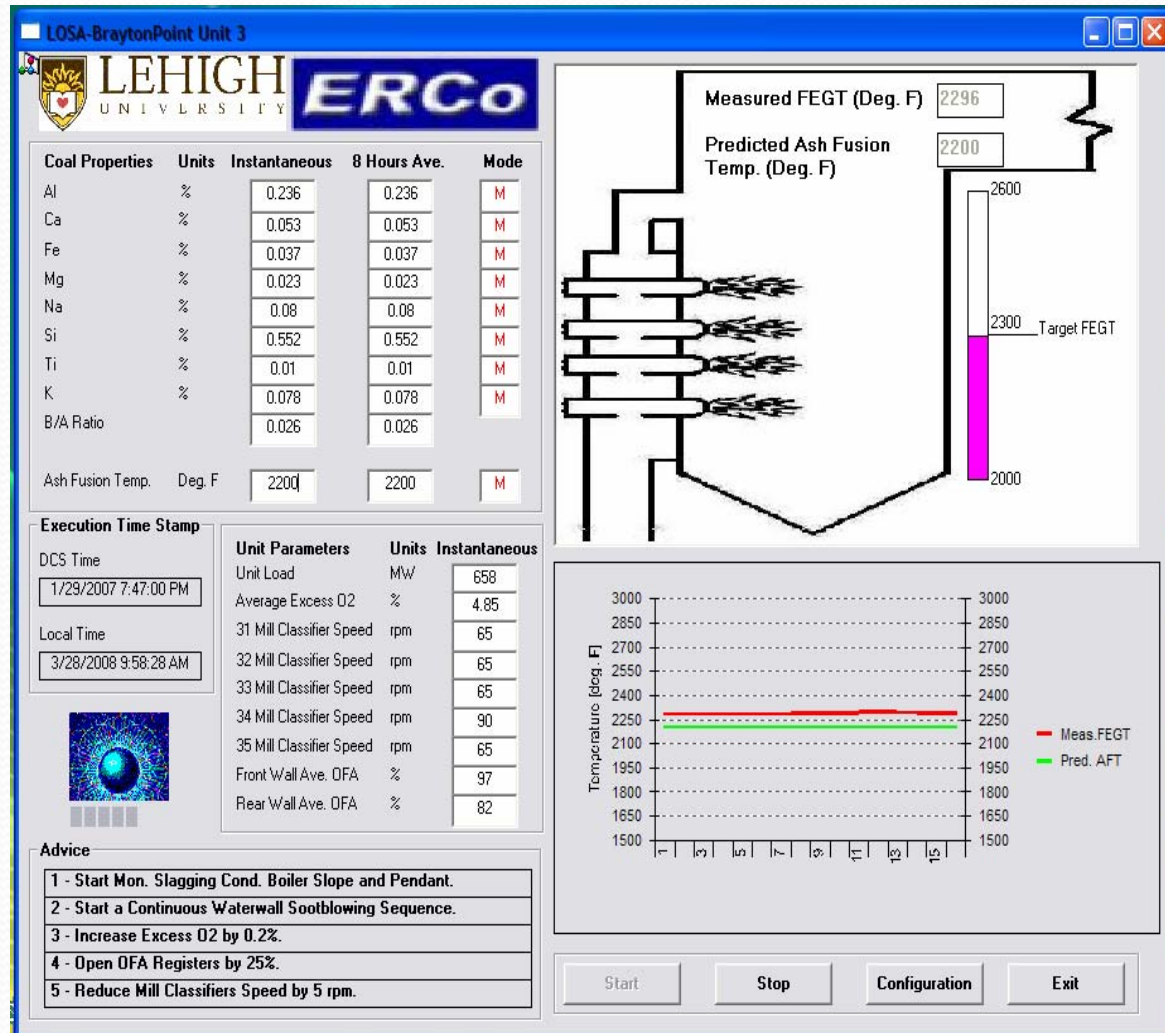


Artificial Neural Network Modeling

Slagging Index Prediction Model



LIBS-Based On-Line Advisory Software



Operator Use of LIBS and LOFA

- Optimize coal yard operation:
 - Fuel blend
 - Fuel distribution
- Optimize boiler control settings
- Optimize sootblowing operation
- Fuel conditioning (additives)
- Additional actions (load cycling, gas firing)

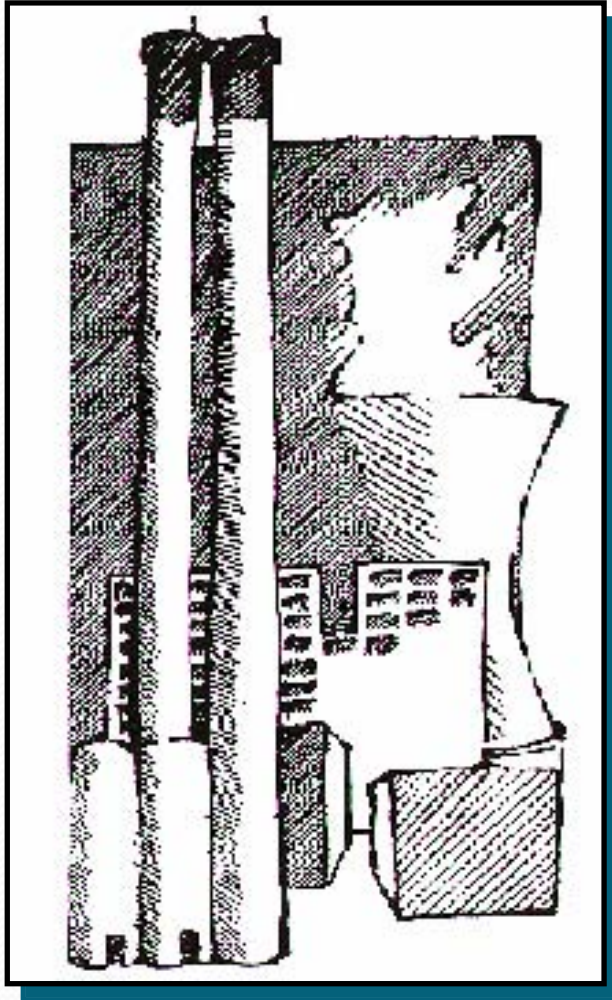
Conclusions

- **Completed Projects:** Performed study and tests using LIBS for coal mineral analysis and slagging propensity prediction.
 - Feasibility Study
 - Laboratory Tests
 - Brayton Point Field Tests
- LIBS-AI technology was shown to calculate coal properties with good accuracy and precision.
- **Current Project:** Development of an on-line LIBS sampling (ASTM Compliant) and analysis system. (DOE STTR Phase 1)
- **Future Project:** Field demonstration of a fully integrated sampling, analysis, on-line advisory system. (DOE STTR Phase 2 and a GENCO Consortium)

Questions ...



ERC Contact Information



Dr. Carlos E. Romero
(cerj@lehigh.edu)

or

Mr. John W. Sale
(jws3@lehigh.edu)

Lehigh University
Energy Research Center
117 ATLSS Drive
Bethlehem, PA 18015-4729

Telephone: (610) 758-4090

Fax: (610) 758-5959

www.lehigh.edu/energy