COAL SLAGGING AND REACTIVITY TESTING

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ABSTRACT

Union Fenosa's La Robla I Power Station is a 270-MW Foster Wheeler arch-fired system. The unit is located at the mine that provides a portion of the semianthracitic coal. The remaining coals used are from South Africa, Russia, Australia, and China. The challenges at the La Robla I Station stem from the various fuels used, the characteristics of which differ from the design coal. The University of North Dakota Energy & Environmental Research Center (EERC) and the Lehigh University Energy Research Center (LUERC) undertook a program to assess problematic slagging and unburned carbon issues occurring at the plant.

Full-scale combustion tests were performed under baseline conditions, with elevated oxygen level and with redistribution of air during a site visit at the plant. During these tests, operating information, observations and temperature measurements, and coal, slag deposit, and fly ash samples were obtained to assess slagging and unburned carbon.

The slagging in almost all cases appeared due to elevated temperatures rather than fuel chemistry. The most severe slagging occurred when the temperature at the sampling port was in excess of 1500°C, with problematic slagging where first-observed temperatures exceeded 1350°C. The presence of anorthite crystals in the bulk of the deposits analyzed indicates that the temperatures were in excess of 1350°C, consistent with temperature measurements during the sampling period.

Elevated temperatures and "hot spots" are probably the result of poor mill performance, and a poor distribution of the coal from the mills to the specific burners causes elevated temperatures in the regions where the slag samples were extracted. A contributing cause appeared to be poor combustion air mixing and heating, resulting in oxygen stratification and increased temperatures in certain areas. Air preheater plugging was observed and reduces the temperature of the air in the windbox, which leads to poor combustion conditions, resulting in unburned carbon as well as slagging.

A second phase of the project involved advanced analysis of the baseline coal along with an Australian coal fired at the plant. These analysis results were used in equilibrium thermodynamic modeling along with a coal quality model developed by the EERC to assess slagging, fouling, and opacity for the coals. Bench-scale carbon conversion testing was performed in a drop-tube furnace to assess the reactivity of the coals.

The Australian coal had a higher mineral content with significantly more clay minerals present than the baseline coal. The presence of these clay minerals, which tend to melt at relatively low temperatures, indicated a higher potential for problematic slagging than the baseline coal. However, the pyritic minerals, comprising over 25% of the baseline mineral content, may form sticky iron sulfides, leading to severe slagging in the burner region if local areas with reducing conditions exist.

Modeling results indicated that neither would present significant fouling problems. The Australian coal was expected to show slagging behavior much more severe than the baseline coal except at very high furnace temperatures. However, the baseline coal was predicted to exhibit opacity

problems, as well as have a higher potential for problematic calcium sulfate-based low-temperature fouling.

The baseline coal had a somewhat higher reactivity than the Australian coal, which was consistent with both the lower average activation energy for the baseline coal and the greater carbon conversion at a given temperature and residence time. The activation energy of the baseline coal showed some effect of oxygen on the activation energy, with E_a increasing at the lower oxygen concentration, but may be due to the scatter in the baseline coal kinetic values at the higher oxygen level tested.

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COAL SLAGGING AND REACTIVITY TESTING

EXPERIMENTAL

Analyses were performed on the baseline La Robla and the imported Australian coals to determine physical and chemical characteristics. The analyses performed included proximate–ultimate analysis; determination of bulk ash chemistry by x-ray fluorescence analysis; and determination of mineral grain size, composition, and association using computer-controlled scanning electron microscopy (CCSEM) analysis.

In order to determine the size, abundance, and association of mineral grains in both high- and low-rank coals, CCSEM and automated image analysis are the preferred techniques used to analyze polished cross sections of coal epoxy plugs. The CCSEM technique is used to determine the size, shape, quantity, and quantitative composition of mineral grains in coals. The key components of the CCSEM system that make it possible to image, size, and analyze inorganic particles are the backscatter electron detector, digital beam control, and the ultrathin window energy-dispersive x-ray detector. Backscatter electron imaging is used for CCSEM because the intensity of the backscattered electrons is a function of the average atomic number of the features on or near the surface. Since the mineral particles appear brighter relative to the lower atomic number background of the matrix, a distinction can be made between coal, mounting media, and mineral grains. The electron beam is programmed to scan over the field of view and locate the bright inclusions that correspond to mineral or ash species. On finding a bright mineral grain, the grain is sized, the center is located, and an energy-dispersive spectrum (EDS) is collected at that point for 2 seconds. The EDS provides the chemical composition of the grain. Software classifies the mineral grains based on the EDS elemental composition and size. The parameters used to identify the minerals are based on published compositions of known minerals. The image analysis determines the mineral grain size and whether the mineral grain is included (bound in the coal structure) or excluded (existing as a free mineral grain not associated with the coal structure).

RESULTS AND DISCUSSION

Tables 1 and 2 contain the proximate–ultimate and bulk ash chemistry results. A summary of the CCSEM analysis results are given in Table 3, with the complete CCSEM analysis results tabulated in Appendix A.

Both coals are typical anthracites, with relatively low moisture and volatile matter content, and high fixed carbon and heating values. The Australian coal analysis indicated an ash content approximately twice that of the baseline coal.

The bulk chemistry of the baseline coal shows a lower silica content along with higher calcium and sulfur content. The high sulfur content indicates that the baseline coal contains significantly more pyritic minerals (pyrite, pyrrhotite, and oxidized pyrrhotite) than does the Australian coal. The Australian coal also has a higher sodium content (1.33% versus 0.17% for the baseline coal).

Table 1. Proximate and Ultimate Analysis

	Baseline Coal	Australian Coal
Proximate Analysis, as-received wt%		
Moisture	12.5	7.2
Volatile Matter	12.1	12.85
Fixed Carbon	68.59	66.57
Ash	6.81	13.39
Ultimate Analysis, as-received wt%		
Hydrogen*	4.03	3.82
Carbon	64.57	71.31
Nitrogen	1.43	1.69
Sulfur	1.88	0.72
Oxygen**	21.27	9.07
Ash	6.81	13.39
Higher Heating Value		
Btu/lb	10,398	11,963
KJ/kg	24,186	27,826

* Includes hydrogen from moisture.

** Includes oxygen from moisture.

The Australian coal has a much higher mineral content in general (13.4% versus 6.8%), and of that, the CCSEM analysis indicates that nearly half of the ash content are clay minerals (kaolin) which tend to melt at relatively low temperatures. Also, a majority of these clay minerals are included within the coal particles and will be exposed to a higher temperature as the coal combusts than the excluded clay minerals in the baseline coal. The baseline coal has a low clay mineral content and needs higher temperatures to liquefy a major portion of the mineral content. The Australian coal would thus be expected to have a higher slagging potential in the boiler than the baseline coal. However, the pyritic minerals comprising over 25% of the baseline mineral content can form sticky iron sulfides leading to severe slagging in the burner region if low oxygen concentration produces local areas with reducing conditions.

PREDICTION OF FOULING AND SLAGGING PERFORMANCE

The analysis results were used in the PCQuest fireside performance model as well as a commercial equilibrium thermodynamic model, FACT (Facility for the Analysis of Chemical Thermodynamics) to predict the fouling and slagging performance of the coals in a boiler.

Table 2. Coal Bulk Ash Chemistry, wt%

Oxide	Baseline Coal	Baseline Coal (duplicate)	Baseline Coal (average)	Australian Coal
SiO ₂	36	35.7	35.85	46.4
Al ₂ O ₃	22.9	22.6	22.75	24.5
Fe ₂ O ₃	12.1	12.2	12.15	11.6
TiO ₂	0.73	0.73	0.73	0.92
P ₂ O ₅	1.03	1.03	1.03	1.87
CaO	11.4	11.6	11.5	6.41
MgO	1.6	1.6	1.6	1.77
Na ₂ O	0.18	0.16	0.17	1.33
K ₂ O	1.8	1.8	1.8	1.14
SO ₃	12.2	12.6	12.4	4.02
Sulfur-Free Basis				
SiO ₂	41.03	40.84	40.93	48.36
Al ₂ O ₃	26.1	25.85	25.98	25.54
Fe ₂ O ₃	13.79	13.96	13.87	12.09
TiO ₂	0.83	0.84	0.83	0.96
P ₂ O ₅	1.17	1.18	1.18	1.95
CaO	12.99	13.27	13.13	6.68
MgO	1.82	1.83	1.83	1.84
Na ₂ O	0.21	0.18	0.19	1.39
K ₂ O	2.05	2.06	2.06	1.19

PCQUEST Description

PCQUEST is an empirical model providing relative ranking of coal performance. Some general boiler parameters are used in the model to account for the type of firing (pulverized coal or cyclone boiler) and the control device (electrostatic precipitator [ESP] or baghouse). Boiler load is taken to be 100% of the maximum continuous firing rate.

The slagging index is a measure of slagging propensity on walls in the radiant section of the boiler. Depending on the furnace exit-gas temperature (FEGT), the slagging region may extend to include platen superheater and reheater surfaces suspended over the furnace box and surfaces at the entrance to the convective pass.

The high-temperature fouling index is a measure of fouling occurring at the front part of the convective pass in the secondary superheater and reheater region. Such fouling is primarily silicate-based and strongly dependent on the FEGT.

Table 3. Summary of CCSEM Data, wt%

Mineral	Baseline Coal Total	Baseline Coal % Excluded	Australian Coal Total	Australian Coal % Excluded
Quartz	3.2	96.1	8.9	26.7
Iron Oxide	2.3	78.7	8.4	76.8
Rutile	0	72.3	1.6	27.2
Calcite	6.8	90.3	11	76.3
Dolomite	0.1	66.0	1.2	47.3
Ankerite	6.4	88.4	1.0	95.6
Kaolinite	3.4	79.4	9	33
Montmorillonite	2.0	95.3	8.1	23.7
Potassium Aluminosilicate	16.8	89.4	10.4	55.1
Iron Aluminosilicate	0.4	99.4	18.5	14.9
Mixed Aluminosilicate	2.5	94.7	0.7	32.7
Pyrite	2.6	83.5	0	0
Pyrrohotite	24	72.6	3.9	73.4
Apatite	0.5	58.8	3.8	11.8
Silica-Rich	0.4	92.6	1.7	42.4
Unknown	25.3	77.7	10.2	29.1

The low-temperature fouling index is a measure of fouling occurring in the primary superheater and economizer region of the convective pass. Such deposition is primarily calcium-based, forming smooth, very hard calcium sulfate deposits.

The opacity index provides an indication of the difficulty of ash collectability, based on the relative abundance of fine hard-to-collect and organically bound minerals in the coal. This value is indicative only of the difficulty of collecting fine ash, in this case reflecting the resistivity of the ash. A well-functioning collection device may effectively control even apparently fine particulate emissions.

The indices are on a scale of 0–100, with 0–33 being low, 34–66 being medium, and 67–100 being a high or severe value. The resolution of the calculations is such that differences of 3–4 index units indicate effectively the same performance.

FACT Description

FACT is an integrated thermodynamic database coupled to programs developed to calculate multicomponent, multiphase equilibria based on a minimization of Gibbs free energy. Once the initial system composition and pressure are set, FACT determines equilibrium concentrations of solid, liquid, and gas species over a specified temperature range. It should be noted that FACT calculates equilibrium concentrations independently at each temperature. Depending on the kinetics

of the reactions occurring, these equilibrium concentrations may or may not be achieved. FACT is also constrained by the number of elements selected as input and the compounds available and selected to be considered in the calculations from the thermodynamic database.

The sample analyses used in the FACT calculations consisted of the bulk ash chemistry and estimated ultimate analyses. The bulk ash chemistry analyses were renormalized excluding SO_3 , since SO_3 is also accounted for in the ultimate analysis. A calculation was then performed to determine the amount of air (oxygen and nitrogen) required to combust an amount of coal containing 1 gram of ash at 20% excess air. Although the excess air and combustion products, N_2 , O_2 , CO_2 , H_2O , NO_2 , and SO_2 , are entered along with the coal ash chemistry for convenience, FACT determines the equilibrium amounts of gas, liquid, and solid compounds as a function of temperature based only on the amount of each element entered.

Calculations were performed at 25°C intervals from 500° to 1500°C. Note that the calculation at each temperature is independent of the previous or subsequent calculations and that each calculation represents an equilibrium condition that may not be kinetically or physically achieved. The compounds considered were approximately 30 major and minor gas species of highest concentration; a silicate-based liquid slag which is noted as Slag C; a solid calcium–magnesium sulfate solution, SCMO, which is indicative of potential low-temperature calcium-based fouling; and all pure solid species in the FACT database.

Calculations were performed on a weight basis to determine the percentage of liquid phases ($100 \times [\text{Slag C solution}] / [\text{Slag C solution} + \text{all solid phases}]$) as a function of temperature. A second calculation was performed on a mole basis to provide input for viscosity calculations. Viscosities for the liquid-phase material (Slag C solution) as a function of temperature were calculated using a modified form of the Urbain equation in a spreadsheet for each sample. The results of the FACT calculations are given in Appendix B, which contains numerical listings of viscosity, liquid phases, and the solid calcium–magnesium sulfate solution as a function of temperature.

Both the viscosity and the amount of liquid phases present are important in predicting the amount of fouling that can occur. An empirical relationship developed from pilot-scale fouling test data where the rate of fouling depositions at a FEGT of 1200°C can be used to estimate the relative severity of deposition:

Deposition rate in grams deposited per kilogram ash fed =

$$2.691 \times (\text{percent liquid phases} / \text{absolute value}(\log_{10} \text{viscosity})) - 3.657$$

The deposition rates for the coals are also given in Appendix B. Although these rates may not accurately reflect the actual deposition experienced in a full-scale boiler, they give an indication of the relative fouling behavior.

PCQUEST PREDICTION RESULTS

The PCQUEST index results for the coals are given in Table 4. Both coals are predicted to have low-temperature fouling behavior. The Australian coal is expected to show a somewhat higher level of high-temperature fouling than the baseline coal, as well as significantly higher and more severe slagging behavior. The baseline coal is predicted to exhibit severe opacity problems, although an effectively operating ESP may reduce stack particulate emissions to an acceptable level. In summary, the baseline coal is predicted to have problematic opacity and the Australian coal problematic slagging.

Table 4. PCQUEST Results

Index	Baseline Coal	Australian Coal
Low-Temperature Fouling	6	6
High-Temperature Fouling	5	25
Slagging	9	76
Opacity	100	33

FACT PREDICTION RESULTS

Figure 1 shows the FACT predictions of the percentage of liquid mineral phases as a function of temperature. At about 925°C, liquids begin to form in both coals. This is due to the clay mineral

Figure 1. Percentage of liquid mineral phases as a function of temperature.

content in each coal. The Australian coal has a much higher mineral content with nearly half being clay minerals, which tend to melt at relatively low temperatures. This is reflected in the higher percentage of liquid phases for the Australian coal. However, the viscosity of the liquid-phase material in the Australian coal is higher than that of the baseline coal, as seen in Figure 2. Figure 3 shows the deposition rate, which takes into account both the percentage of liquid phases and the liquid-phase viscosity. The Australian coal is predicted by the FACT calculations to have a significantly higher deposition rate than the baseline coal at all but the highest temperatures (near 1500°C). This is in agreement with the PCQUEST prediction of significantly higher slagging potential for the Australian coal.

Figure 4 shows the percentage of solid sulfates predicted by FACT, which indicate that the baseline coal will form a significantly higher percentage of sulfates (approximately 34% versus 20%) than the Australian coal. This indicates that low-temperature fouling in the reheater and economizer regions of the boiler will be greater for the baseline coal as a result of the higher sulfur and calcium content. The formation of low-temperature sulphate phases may also contribute to the air preheater plugging that was noted during the La Robla Unit 1 field testing.

Comparison with Field Test Observations

Observations of slag and deposit formations and temperature measurements were made during the field testing at La Robla Unit 1 on August 20–22, 2002. These observations were limited to ports on Levels 1.5, 2, 6, and 6.5. It was not certain whether the baseline, Australian, other coals, or coal blends were being fired at the time the observations were made. The observations made at Level 6, as well as plant-operating experience, indicated that high-temperature fouling was not a significant

Figure 2. Viscosity of liquid-phase material.

Figure 3. Predicted relative deposition rate.

Figure 4. Percentage of solid sulfates.

issue. Some deposition was occurring lower in the convective pass but was controllable with sootblowing. This is in agreement with the PCQUEST prediction of a low index value for high-temperature fouling. Significant slagging was observed in the lower region of the boiler at Levels 1.5 and 2, along with very high gas temperatures. These observations are again in agreement with the PCQUEST prediction of a slagging index in the “severe” range (for the Australian coal) as well as the FACT predictions of high deposition rates at these temperatures. More details can be found in the previous field testing report attached as Appendix C.

COAL REACTIVITY TESTING

Drop-Tube Furnace System

The drop-tube furnace (DTF) is a laboratory-scale, entrained-flow, tube furnace with the ability to combust coal and produce ash under closely controlled conditions. Combustion parameters such as initial hot-zone temperature, residence time, and gas cooling rate can be closely controlled and monitored.

The furnace assembly consists of a series of vertically oriented tube furnaces illustrated in Figure 5. These furnaces possess a total of four independently controlled, electrically heated zones. Each of these furnaces can be used separately or in conjunction with the other furnaces. This allows for maximum flexibility and precise control over combustion conditions.

Coal and primary and secondary air are introduced into the furnace system by a preheat injector. This system injects ambient temperature primary air (1 L/min) and coal into the furnace from a water-cooled probe assembly at the center of the tube. Secondary air (4 L/min) is typically heated to 1000°C and introduced into the furnace through a mullite flow straightener. Thus, the material to be combusted is introduced into the top of the furnace, along with preheated secondary air, and travels down the length of the furnace in a laminar flow regime. Various sampling probes or collection devices can be used with the DTF to collect ash samples.

Downstream of the sampling probe and collection filter, the combustion gas is cooled and passes through a filter before it enters a diaphragm pump. The pump is designed so that no air can leak into the sampling gas. The gas leaving the positive pressure side of the pump is passed through a flowmeter, which measures the volume of gas being pulled through the probe. After the flowmeter, part of the gas is directed through carbon monoxide, carbon dioxide, and oxygen analyzers. The concentrations of these gases can be read directly from the digital readouts of the analyzers as well as logged by a personal computer for later data processing.

The coal feed system is designed to feed particles of various sizes in the pulverized coal range, which are entrained in the primary air flow, at rates of 0.05–0.5 grams per minute. The basic apparatus shown in Figure 6 consists of a pressurized cylinder in which a container filled with coal is placed. A rotating brush and a stirrer attached to a variable-speed motor feed the coal from the container into a funnel where it is transported through the feed tubing into the furnace injector by the carrier gas. The coal feeder is mounted on a top-loading balance to monitor the feed rate.

Figure 5. Drop-tube furnace.

Figure 6. Coal feed system.

A short residence-time probe is used to collect ash samples at any residence time. The probe consists of a series of four concentric, water-cooled, steel tubes. The outer shell is for introducing the quench gas at the top of the probe. The combustion products pass through the innermost shell, and the remaining shells carry the cooling water. The probe is covered with a 2-inch-outside-diameter alumina insulating cylinder (Figure 7).

The probe is inserted in the bottom of the furnace a set distance from the injector, calculated using the desired residence time. The quench gas and vacuum are turned on. The coal is fed through the preheat injector, the combustion products are quenched upon entering the probe, and the residue char or ash is collected on a filter attached to the probe's innermost shell.

CARBON CONVERSION MEASUREMENTS

Introduction

The anthracite fuels were fired in the DTF at various temperatures and residence times to calculate conversion rates. The combustion runs were performed at 5 temperatures and with residence times allowing partial to complete conversion. The initial oxygen concentrations for testing were set at 20.9% atmospheric air and 10.0% oxygen for the tests. Char/ash samples were collected and gas analyses recorded during each test. Table 5 gives the run conditions for each test. The carbon conversion for the fuels burned was determined from the difference between the weight of the fuel fed and the weight of the residue collected. Carbon conversion was also calculated from the CO and CO₂ gas concentration. For simplicity in describing the methods used, the two methods

Figure 7. Short residence-time probe.

Table 5. Carbon Conversion Test Conditions

Test Number	Furnace		Particle Diameter, μm	Residence Time, s	Gas Flow, L/min	Ambient Temperature, $^{\circ}\text{C}$	Atmospheric Pressure, atm	Feed Time, min	Fuel Fed, g	Residue Collected, g	CO_2 , %	CO , ppm	O_2 , %	
	Temperature, $^{\circ}\text{C}$	Fuel												
1162	Australian coal	900	21.0	12.95	2.39	7.00	24	737.50	10.0	1.64	1.2670	0.35	404	19.50
1186	Australian coal	900	21.0	12.95	2.87	7.00	22	743.80	10.0	1.60	1.0071	1.11	232	18.90
1185	Australian coal	900	21.0	12.95	3.34	7.00	22	743.80	10.0	1.59	0.8067	1.90	130	18.10
1156	Australian coal	1000	21.0	12.95	2.21	7.00	23	737.80	15.0	1.61	0.9732	0.45	156	19.40
1160	Australian coal	1000	21	12.95	2.58	7.00	24	737.50	10.0	1.59	0.6912	2.44	91	17.50
1161	Australian coal	1000	21.0	12.95	3.23	7.00	24	737.50	10.0	1.61	0.5217	3.51	58	16.60
1187	Australian coal	1100	21.0	12.95	2.05	7.00	22	743.10	10.0	1.61	0.6004	2.87	74	17.10
1189	Australian coal	1100	21.0	12.95	2.29	7.00	22	743.10	10.0	1.59	0.4845	3.18	62	16.60
1188	Australian coal	1100	21.0	12.95	2.52	7.00	22	743.10	10.0	1.62	0.4100	3.82	51	16.10
1157	Australian coal	1200	21.0	12.95	1.92	7.00	24	737.71	15.0	2.33	0.5526	3.88	0	16.30
1190	Australian coal	1200	21.0	12.95	2.19	7.00	22	743.10	10.0	1.64	0.3020	4.27	32	14.70
1159	Australian coal	1200	21.0	12.95	2.46	7.00	24	737.71	20.0	3.18	0.5049	4.90	18	15.60
1158	Australian coal	1200	21.0	12.95	3.08	7.00	24	737.71	15.0	2.40	0.3155	4.83	12	15.30
1228	Baseline coal	800	21.0	18.76	2.51	7.00	23	731.20	10.0	1.66	1.4315	0.01	1226	20.70
1229	Baseline coal	800	21.0	18.76	3.53	7.00	23	731.20	10.0	1.68	1.1403	0.75	324	19.00
1225	Baseline coal	900	21.0	18.76	2.30	7.00	23	731.20	10.0	1.74	1.0984	1.00	176	18.70
1227	Baseline coal	900	21.0	18.76	2.85	7.00	23	731.20	10.0	1.72	0.8719	2.07	139	17.50
1226	Baseline coal	900	21.0	18.76	3.39	7.00	23	731.20	10.0	1.71	0.7241	2.44	103	17.10
1191	Baseline coal	1000	21.0	18.76	2.18	7.00	22	737.00	10.0	1.71	0.6721	3.03	89	17.00
1193	Baseline coal	1000	21.0	18.76	2.73	7.00	22	737.00	10.0	1.72	0.4986	3.55	55	16.30
1192	Baseline coal	1000	21.0	18.76	3.28	7.00	22	737.00	10.0	1.70	0.4265	3.90	47	16.00
1222	Baseline coal	1100	21.0	18.76	1.98	7.00	22	736.95	10.0	1.67	0.4541	2.80	56	17.00
1224	Baseline coal	1100	21.0	18.76	2.59	7.00	22	736.95	10.0	1.56	0.3327	3.40	25	16.20
1223	Baseline coal	1100	21.0	18.76	3.19	7.00	22	736.95	10.0	1.57	0.2816	3.35	14	16.20
1290	Baseline coal	1000	10.5	12.24	2.15	7.00	22	736.90	10.0	1.29	0.8924	0.31	118	9.60
1291	Baseline coal	1000	10.5	12.24	3.33	7.00	21	739.30	10.0	1.23	0.6088	0.89	47	8.80
1292	Baseline coal	1000	10.5	12.24	4.00	7.00	21	739.30	10.0	1.30	0.5506	1.20	41	8.30
1293	Baseline coal	1100	10.5	12.24	2.00	7.00	21	739.30	10.0	1.25	0.6931	0.68	76	8.80
1295	Baseline coal	1100	10.5	12.24	2.61	7.00	21	739.30	10.0	1.30	0.5524	1.23	40	8.10
1294	Baseline coal	1100	10.5	12.24	3.23	7.00	21	739.30	10.0	1.27	0.3940	1.57	30	8.00
1296	Baseline coal	1200	10.5	12.24	1.87	7.00	22	738.60	10.0	1.22	0.5073	1.13	43	8.20
1298	Baseline coal	1200	10.5	12.24	2.19	7.00	22	738.60	10.0	1.26	0.3965	1.33	30	7.90
1297	Baseline coal	1200	10.5	12.24	2.52	7.00	22	738.60	10.0	1.27	0.3331	1.67	23	7.7

will be described hereafter as carbon conversion by the 1) weight loss analysis method or 2) gas analysis method. Table 6 shows the comparison of carbon conversion calculated from the gas analyses (gas carbon conversion %) and the weight loss method (fuel burned). The gas analysis method tended to give generally higher carbon conversions and was more erratic than the weight loss method. The results of the weight loss method were deemed to be more reliable, and reaction rates subsequently calculated using the weight loss results for the fuels.

Weight Loss Method

The amount of fuel burned was calculated from the weight loss of the coal fed in the DTF. The amount of ash fed was determined from the percentage of ash in the fuel, derived from proximate analysis multiplied by the amount of fuel fed. The char or residue that is left from the test was collected on a filter and weighed. The percent carbon conversion was then calculated by:

$$\% \text{ carbon conversion} = \left| 1 - \frac{\text{g char collected} - \text{g ash fed}}{\text{g coal fed} - \text{g ash fed} - \text{g water fed}} \right| \quad [\text{Eq. 1}]$$

Gas Analysis Method

The gas flow rate and the Ideal Gas Law, $PV = nRT$, were used to convert the concentrations of CO_2 and CO in the gas stream into molar quantities. The molar feed rate of carbon was calculated from the coal feed rate and the percentage of carbon in the ultimate analysis of the fuel. These quantities were used to determine the percentage of carbon conversion by gas analysis indicated in Table 2. The equations are as follows:

$$\text{moles } \text{CO}_2 = (\text{total gas flow rate}) \times (\% \text{CO}_2/100) \times (P/760\text{mmHg})/R \times T_K \quad [\text{Eq. 2}]$$

$$\text{moles } \text{CO} = (\text{total gas flow rate}) \times (\% \text{CO}/100) \times (P/760\text{mmHg})/R \times T_K \quad [\text{Eq. 3}]$$

where P is the barometric pressure (mmHg), R is the universal gas constant (0.082 L atm/mole K), and T_K is the gas temperature in Kelvin. The carbon feed rate is calculated by:

$$\text{molar feed rate} = (\% \text{ carbon}/100) \times (\text{coal feed rate}) \times (1 \text{ mole C}/12 \text{ g C}) \quad [\text{Eq. 4}]$$

and the percent carbon conversion is calculated by:

$$\% \text{ carbon conversion} = ([\text{moles } \text{CO}_2 + \text{moles } \text{CO}]/[\text{molar feed rate}]) \times 100\% \quad [\text{Eq. 5}]$$

Reaction Rates for the Coals

Data Reduction

Carbon conversion testing was performed at specific probe insertion distances, resulting in variable residence times depending on gas temperature. Linear regressions were performed on each

Table 6. Carbon Conversion Test Results

Test Number	Fuel	Temperature, °C	Oxygen, %	Residence Time, s	Conversion	
					Fuel Burned, %	Conversion Gas Conversion, %
1162	Australian coal	900	20.9	1.79	21.99	10.89
1186	Australian coal	900	20.90	2.15	39.57	32.88
1185	Australian coal	900	20.90	2.50	54.55	55.86
1156	Australian coal	1000	20.90	1.71	42.63	19.91
1160	Australian coal	1000	20.90	2.00	63.47	70.43
1161	Australian coal	1000	20.90	2.50	77.06	99.86
1187	Australian coal	1100	20.90	1.63	71.06	82.90
1189	Australian coal	1100	20.90	1.82	79.43	92.95
1188	Australian coal	1100	20.90	2.00	85.77	109.53
1157	Australian coal	1200	20.90	1.56	87.73	114.25
1190	Australian coal	1200	20.90	1.78	94.24	120.87
1159	Australian coal	1200	20.90	2.00	97.35	141.01
1158	Australian coal	1200	20.90	2.50	100.70	138.11
1228	Baseline coal	800	20.90	1.78	13.90	3.75
1229	Baseline coal	800	20.90	2.50	34.03	21.21
1225	Baseline coal	900	20.90	1.70	39.24	26.64
1227	Baseline coal	900	20.90	2.10	52.87	55.18
1226	Baseline coal	900	20.90	2.50	62.02	65.26
1191	Baseline coal	1000	20.90	1.66	65.36	81.86
1193	Baseline coal	1000	20.90	2.08	76.67	95.22
1192	Baseline coal	1000	20.90	2.50	80.94	105.80
1222	Baseline coal	1100	20.90	1.55	78.64	77.38
1224	Baseline coal	1100	20.90	2.03	85.07	100.46
1223	Baseline coal	1100	20.90	2.50	88.79	98.32
1290	Baseline coal	1000	10.50	1.62	32.60	11.49
1291	Baseline coal	1000	10.50	2.50	54.18	33.72
1292	Baseline coal	1000	10.50	3.00	62.01	42.94
1293	Baseline coal	1100	10.50	1.55	47.66	25.50
1295	Baseline coal	1100	10.50	2.02	61.86	44.01
1294	Baseline coal	1100	10.50	2.50	74.44	57.42
1296	Baseline coal	1200	10.50	1.48	62.86	42.92
1298	Baseline coal	1200	10.50	1.74	73.95	48.84
1297	Baseline coal	1200	10.50	2.00	79.69	60.79

set of weight loss data to obtain equations of carbon conversion versus residence time. These equations were then used to calculate carbon conversions for residence time of 1.75, 2.00, 2.25, and 2.50 seconds, as given in Table 7. These values were subsequently used in the following kinetic calculations.

Table 7. Regression Analysis of Carbon Conversion

			Time, s				
			1.5	1.75	2	2.25	2.5
r^2	m	b	Conversion, %				
0.9985831	45.873429	-59.77052	20.51	31.98	43.44	54.91	66.38
0.9271418	41.784954	-24.92398	37.24	47.68	58.13	68.58	79.02
0.9959006	39.803203	6.4458037	66.15	76.10	86.05	96.00	NA
0.8705846	12.812171	69.892883	89.11	92.31	95.52	98.72	NA
NA ¹	27.958	-35.865	6.07	13.06	20.05	27.04	34.03
0.987267	28.483289	-8.438198	34.29	41.41	48.53	55.65	62.77
0.9364261	18.556624	35.725797	63.56	68.20	72.84	77.48	82.12
0.9785321	10.692117	62.495539	78.53	81.21	83.88	86.55	89.23
0.9888134	21.680209	-1.855705	30.66	36.08	41.50	46.92	52.34
0.9983024	28.183586	4.2932201	46.57	53.61	60.66	67.71	74.75
0.9675028	32.375212	15.835052	64.4	72.49	80.59	88.68	96.77

¹ Not applicable.

Kinetic Calculations and Modeling

Kinetic values were determined for the carbon loss data using the formulation of Field (1, 2) as modified by Nsakala and others (3). The calculations are based on surface area, employing a shrinking core model. Volatile evolution was not included in the model since the anthracite coals contain little volatile matter, and the devolatilization time is expected to be short in comparison with the char-burning stage.

From the formulation of Nsakala and others (3), the rate of carbon removal per unit surface area, q , in $\text{g cm}^{-2} \text{sec}^{-1}$ is given in integrated form by:

$$q = 3(1 - U^{1/3}) / (S_0 t) \quad [\text{Eq. 6}]$$

where U is the fraction of unburned material, t is the residence time in sec, S_0 is the initial surface area in cm^2/g , and:

$$S_0 = 6/(Xp) \quad [\text{Eq. 7}]$$

where X is the original particle diameter in centimeters, and p is the particle density in g/cm^3 .

The overall reaction rate coefficient, K , is defined as:

$$K = q/P_g \quad [\text{Eq. 8}]$$

where P_g is the partial pressure of oxygen in the gas in atm.

The overall reaction rate coefficient, K , depends on the rate of oxygen diffusion to the particle surface and the rate of reaction of oxygen at the surface:

$$1/K = 1/K_{\text{diff}} + 1/K_s \quad [\text{Eq. 9}]$$

where K_{diff} is the diffusional reaction rate coefficient, and K_s is the surface reaction rate coefficient. Units on K_{diff} and K_s are $\text{g}/(\text{cm}^2 \text{ sec atm})$.

The diffusional reaction rate coefficient, K_{diff} , in $\text{g}/(\text{cm}^2 \text{ sec atm})$ is given by:

$$K_{\text{diff}} = (2 \times \text{AW Carbon}) \phi D / (\bar{X} R T_m) \quad [\text{Eq. 10}]$$

where AW is the atomic weight of carbon (12 g/mole); ϕ is the molar ratio of product gases to reactant gases (taken as equal to 2 for the reaction $\text{O}_2 + 2\text{C} \rightarrow 2\text{CO}$); D is the binary diffusion coefficient of oxygen in nitrogen in cm^2/sec ; $\bar{X}$ is the average particle diameter in cm at time t ; R is the ideal gas constant, $82.06 \text{ cm}^3 \text{ atm}/\text{mole K}$; and T_m is the temperature of the boundary layer in K (taken as T_g when calculation was based on gas temperature and $[(T_g + T_{\text{particle}})]/2$ when calculation was based on calculated particle temperature).

The surface reaction rate constant, K_s , is traditionally used to determine the apparent activation energy, E_a , and the frequency factor, A , from the relationship:

$$K_s = A \exp (-E_a/RT_g) \quad [\text{Eq. 11}]$$

The particle surface temperature, T_{particle} , is calculated from a heat balance on the particle, assuming steady-state burning conditions and CO as the primary product of the combustion:

$$H_g = H_c + H_r \quad [\text{Eq. 12}]$$

where H_g is the rate of heat generation per unit area in $\text{cal}/(\text{cm}^2 \text{ sec})$; H_c is the rate of heat transfer by conduction in $\text{cal}/(\text{cm}^2 \text{ sec})$; and H_r is the rate of heat transfer by radiation in $\text{cal}/(\text{cm}^2 \text{ sec})$.

The rate of heat generation, H_g , is given by:

$$H_g = q \Delta H \quad [\text{Eq. 13}]$$

where ΔH is the enthalpy of the reaction $\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$.

The rate of heat transfer by conduction is given by:

$$H_c = 2 \lambda (T_{\text{particle}} - T_g)/X \quad [\text{Eq. 14}]$$

where λ is the thermal conductivity of the gas in cal/(cm sec K) and X is the particle diameter in cm at residence time t.

The rate of heat transfer by radiation is given by:

$$H_r = \epsilon \sigma (T_{\text{particle}}^4 - T_{\text{wall}}^4) \quad [\text{Eq. 15}]$$

where ϵ is the emissivity of particle and wall, taken as 0.8; σ is the Stefan–Boltzmann constant, 1.36×10^{-12} cal/cm sec K; and T_{wall} is the furnace wall temperature in K.

A BASIC program was written to calculate the values of q , T_{particle} , K , K_{diff} , and K_s . The program reads a Lotus[®].prn file containing the pertinent input data with the proper spacing format and writes the results of the calculations to a second file compatible with the Lotus[®] import format. Options that allow calculation of kinetic values from carbon conversion by gas or weight analysis will use either furnace, average gas, or collection point gas temperature in the calculation and reference the results to either gas or calculated particle temperature. Temperature-dependent values of heat capacity, thermal conductivity, and diffusion have been taken from those compiled by Mitchell (4). Particle temperature is calculated from Equation 12 and the subsequent ancillary equations by using a simple "brute force" method of calculating the heat balance at increasing 1 K intervals for the particle temperature starting at the gas temperature. The particle temperature is taken to be the temperature at which the heat balance changes sign. Since the enthalpy, conductivity, H_g , H_c , and H_r are all temperature-dependent and must be recalculated for each increment of particle temperature, calculation of the particle temperature accounts for the majority of computational time used.

The values calculated for q , K , K_{diff} , K_s , and $\ln(K_s)$ are given in Table 8. The kinetic values were calculated using carbon conversions based on the weight loss method and average furnace temperature. Linear regressions of the carbon conversion versus actual residence time were first used to first calculate carbon conversion at residence times of 1.50, 1.75, 2.00, 2.25, and 2.50 seconds, which were used in the subsequent kinetic calculations.

Coal Reactivity Testing Results

Arrhenius plots of the coals based on the weight loss method are shown in Figures 8–10. The values of A and E_a determined for the combustion tests are given in Table 9. It is seen that the values at 1.5 seconds for the lowest temperature ($1/T = 8.52 \text{ E-4 K}^{-1}$ for the Australian coal and $1/T = 9.32 \text{ E-4 K}^{-1}$ for the baseline coal) is lower than the general trend for both coals. There is also more scatter in the Australian coal values than for the baseline coal. Omitting the value for the 1.5-second residence time at the lowest temperature, the average A and E_a values are 7.828 s^{-1} and -19805 cal/mole for the Australian coal and 5.990 s^{-1} and -17411 cal/mole for the baseline coal at 20.9% oxygen. The baseline coal at 10.5% oxygen has A and E_a values of 6.143 and -18555 cal/mole . The baseline coal has a somewhat higher reactivity than the Australian coal, which

Table 8. Calculated Kinetic Values

Coal	Furnace		Initial Diameter, μm	Calculated		Calculated Carbon Conversion, %	q	K	K_{diff}	K_s	$\text{Ln } K_s$	1/T, K
	Residence Time, s	Temperature, $^{\circ}\text{C}$		Final Diameter, μm	Conversion, %							
Australian	1.50	900	75	72.67	9.04	9.04	6.969E-005	3.417E-004	0.1430	3.425E-004	-7.9793	8.525E-004
Australian	1.75	900	75	69.48	20.51	20.51	1.415E-004	6.938E-004	0.1496	6.971E-004	-7.2686	8.525E-004
Australian	2.00	900	75	65.96	31.98	31.98	2.027E-004	9.936E-004	0.1576	9.999E-004	-6.9079	8.525E-004
Australian	2.25	900	75	62.02	43.44	43.44	2.585E-004	1.267E-003	0.1676	1.277E-003	-6.6631	8.525E-004
Australian	2.50	900	75	57.51	54.91	54.91	3.136E-004	1.538E-003	0.1807	1.551E-003	-6.4690	8.525E-004
Australian	1.50	1000	75	64.21	37.24	37.24	3.224E-004	1.590E-003	0.1720	1.604E-003	-6.4350	7.855E-004
Australian	1.75	1000	75	60.43	47.68	47.68	3.731E-004	1.840E-003	0.1827	1.858E-003	-6.2880	7.855E-004
Australian	2.00	1000	75	56.11	58.13	58.13	4.235E-004	2.088E-003	0.1968	2.110E-003	-6.1609	7.855E-004
Australian	2.25	1000	75	50.99	68.58	68.58	4.784E-004	2.359E-003	0.2166	2.385E-003	-6.0386	7.855E-004
Australian	2.50	1000	75	44.57	79.02	79.02	5.458E-004	2.691E-003	0.2478	2.720E-003	-5.9069	7.855E-004
Australian	1.50	1100	75	52.27	66.15	66.15	6.793E-004	3.324E-003	0.2206	3.375E-003	-5.6913	7.283E-004
Australian	1.75	1100	75	46.54	76.10	76.10	7.290E-004	3.567E-003	0.2477	3.619E-003	-5.6215	7.283E-004
Australian	2.00	1100	75	38.90	86.05	86.05	8.092E-004	3.960E-003	0.2964	4.014E-003	-5.5181	7.283E-004
Australian	2.25	1100	75	25.65	96.00	96.00	9.833E-004	4.812E-003	0.4495	4.864E-003	-5.3259	7.283E-004
Australian	2.50	1100	75	1.62	100.00	100.00	1.316E-003	6.439E-003	7.1322	6.445E-003	-5.0444	7.283E-004
Australian	1.50	1200	75	35.82	89.11	89.11	1.171E-003	5.731E-003	0.3374	5.830E-003	-5.1448	6.789E-004
Australian	1.75	1200	75	31.89	92.31	92.31	1.104E-003	5.404E-003	0.3789	5.482E-003	-5.2063	6.789E-004
Australian	2.00	1200	75	26.64	95.52	95.52	1.084E-003	5.305E-003	0.4537	5.368E-003	-5.2274	6.789E-004
Australian	2.25	1200	75	17.54	98.72	98.72	1.145E-003	5.602E-003	0.6889	5.648E-003	-5.1765	6.789E-004
Australian	2.50	1200	75	1.62	100.00	100.00	1.316E-003	6.439E-003	7.4762	6.445E-003	-5.0445	6.789E-004
Baseline	1.50	800	75	73.45	6.07	6.07	5.178E-005	2.575E-004	0.1352	2.580E-004	-8.2625	9.320E-004
Baseline	1.75	800	75	71.58	13.06	13.06	9.793E-005	4.870E-004	0.1388	4.888E-004	-7.6237	9.320E-004
Baseline	2.00	800	75	69.61	20.05	20.05	1.351E-004	6.720E-004	0.1427	6.752E-004	-7.3005	9.320E-004
Baseline	2.25	800	75	67.52	27.04	27.04	1.667E-004	8.290E-004	0.1471	8.337E-004	-7.0896	9.320E-004
Baseline	2.50	800	75	65.29	34.03	34.03	1.947E-004	9.684E-004	0.1521	9.746E-004	-6.9334	9.320E-004
Baseline	1.50	900	75	65.20	34.29	34.29	3.274E-004	1.628E-003	0.1617	1.645E-003	-6.4101	8.525E-004
Baseline	1.75	900	75	62.76	41.41	41.41	3.507E-004	1.744E-003	0.1680	1.762E-003	-6.3410	8.525E-004
Baseline	2.00	900	75	60.11	48.53	48.53	3.734E-004	1.857E-003	0.1754	1.877E-003	-6.2782	8.525E-004
Baseline	2.25	900	75	57.20	55.65	55.65	3.967E-004	1.973E-003	0.1844	1.994E-003	-6.2174	8.525E-004
Baseline	2.50	900	75	53.95	62.77	62.77	4.221E-004	2.099E-003	0.1954	2.122E-003	-6.1555	8.525E-004

Continued ...

Table 8. Calculated Kinetic Values (continued)

Coal	Residence Time, s	Furnace Temperature, °C	O ₂ , %	Initial Diameter, µm	Calculated Final Diameter, µm	Calculated Carbon Conversion, %	q	K	K _{diff}	K _s	Ln K _s	1/T, K
Baseline	1.50	1000	20.9	75	53.57	63.56	7.163E-004	3.534E-003	0.2063	3.596E-003	-5.6280	7.855E-004
Baseline	1.75	1000	20.9	75	51.19	68.20	6.821E-004	3.365E-003	0.2159	3.419E-003	-5.6785	7.855E-004
Baseline	2.00	1000	20.9	75	48.57	72.84	6.625E-004	3.269E-003	0.2275	3.317E-003	-5.7088	0.000786
Baseline	2.25	1000	20.9	75	45.63	77.48	6.544E-004	3.229E-003	0.2422	3.273E-003	-5.7222	7.855E-004
Baseline	2.50	1000	20.9	75	42.25	82.12	6.567E-004	3.240E-003	0.2615	3.281E-003	-5.7196	7.855E-004
Baseline	1.50	1100	20.9	75	44.91	78.53	1.006E-003	4.963E-003	0.2589	5.060E-003	-5.2865	7.283E-004
Baseline	1.75	1100	20.9	75	42.96	81.21	9.180E-004	4.530E-003	0.2706	4.607E-003	-5.3802	7.283E-004
Baseline	2.00	1100	20.9	75	40.82	83.88	8.569E-004	4.228E-003	0.2848	4.292E-003	-5.4511	7.283E-004
Baseline	2.25	1100	20.9	75	38.43	86.55	8.149E-004	4.021E-003	0.3025	4.075E-003	-5.5028	7.283E-004
Baseline	2.50	1100	20.9	75	35.68	89.23	7.885E-004	3.891E-003	0.3258	3.938E-003	-5.5372	7.283E-004
Baseline	1.50	1000	10.5	75	66.38	30.66	3.130E-004	3.068E-003	0.1661	3.125E-003	-5.7682	7.855E-004
Baseline	1.75	1000	10.5	75	64.61	36.08	3.236E-004	3.172E-003	0.1707	3.232E-003	-5.7347	7.855E-004
Baseline	2.00	1000	10.5	75	62.73	41.50	3.344E-004	3.277E-003	0.1758	3.340E-003	-5.7019	7.855E-004
Baseline	2.25	1000	10.5	75	60.73	46.92	3.457E-004	3.388E-003	0.1816	3.452E-003	-5.6687	7.855E-004
Baseline	2.50	1000	10.5	75	58.58	52.34	3.578E-004	3.507E-003	0.1882	3.573E-003	-5.6343	7.855E-004
Baseline	1.50	1100	10.5	75	60.86	46.57	5.137E-004	5.029E-003	0.1904	5.165E-003	-5.2658	7.283E-004
Baseline	1.75	1100	10.5	75	58.06	53.61	5.274E-004	5.164E-003	0.1996	5.301E-003	-5.2398	7.283E-004
Baseline	2.00	1100	10.5	75	54.95	60.66	5.461E-004	5.346E-003	0.2109	5.485E-003	-5.2057	7.283E-004
Baseline	2.25	1100	10.5	75	51.45	67.71	5.702E-004	5.582E-003	0.2252	5.724E-003	-5.1630	7.283E-004
Baseline	2.50	1100	10.5	75	47.40	74.75	6.014E-004	5.888E-003	0.2445	6.034E-003	-5.1104	7.283E-004
Baseline	1.50	1200	10.5	75	53.16	64.40	7.935E-004	7.776E-003	0.2288	8.050E-003	-4.8221	6.789E-004
Baseline	1.75	1200	10.5	75	48.78	72.49	8.164E-004	8.001E-003	0.2493	8.266E-003	-4.7956	6.789E-004
Baseline	2.00	1200	10.5	75	43.42	80.59	8.602E-004	8.430E-003	0.2800	8.691E-003	-4.7454	6.789E-004
Baseline	2.25	1200	10.5	75	36.28	88.68	9.376E-004	9.188E-003	0.3351	9.447E-003	-4.6620	6.789E-004
Baseline	2.50	1200	10.5	75	23.89	96.77	1.114E-003	1.092E-002	0.5091	1.116E-002	-4.4958	0.000679

Figure 8. Arrhenius plot of Australian coal at 20.9% oxygen.

Figure 9. Arrhenius plot of baseline coal at 20.9% O₂.

Figure 10. Arrhenius plot of baseline coal at 10.5% oxygen.

Table 9. E_a and A Values from Regression Analysis

Coal	Residence Time, s	O ₂ , %	n	r ²	m	b	A, 1/s atm	E _a , cal/mol
Australian	1.5	20.9	4	0.968	-16,187	6.011	407.722	-32,166
Australian	1.75	20.9	4	0.987	-11,949	3.001	20.101	-23,745
Australian	2.00	20.9	4	0.986	-9905	1.588	4.892	-19,684
Australian	2.25	20.9	4	0.966	-9027	1.071	2.919	-17,938
Australian	2.50	20.9	4	0.924	-8984	1.223	3.399	-17,853
Baseline	1.50	20.9	4	0.930	-14,615	5.655	285.583	-29,043
Baseline	1.75	20.9	4	0.953	-11,086	2.885	17.909	-22,030
Baseline	2.00	20.9	4	0.961	-9161	1.370	3.934	-18,205
Baseline	2.25	20.9	4	0.961	-7869	0.356	1.427	-15,638
Baseline	2.50	20.9	4	0.958	-6929	-0.372	0.689	-13,770
Baseline	1.50	10.5	3	1.000	-8867	1.196	3.307	-17,621
Baseline	1.75	10.5	3	1.000	-8801	1.176	3.241	-17,489
Baseline	2.00	10.5	3	1.000	-8960	1.331	3.787	-17,806
Baseline	2.25	10.5	3	0.998	-9423	1.723	5.6	-18,725
Baseline	2.5	10.5	3	0.992	-10,635	2.693	14.781	-21,134

is consistent with both the lower average activation energy for the baseline coal and the greater carbon conversion at a given temperature and residence time shown in Table 7. Comparison of the activation energy of the baseline coal at 20.9% and 10.5% oxygen shows some effect of oxygen on the activation energy, with E_a increasing at the lower concentration. However, this may be due to the scatter in the baseline coal kinetic values at the higher oxygen level.

CONCLUSIONS

The Australian coal has a higher mineral content with significantly more clay minerals present than the baseline coal. The presence of these clay minerals, which tend to melt at relatively low temperatures, indicates that it will have a higher potential for problematic slagging than the baseline coal. However, the pyritic minerals comprising over 25% of the baseline mineral content may form sticky iron sulfides leading to severe slagging in the burner region if local areas with reducing conditions exist.

Modeling of the combustion behavior of the coals indicates that neither will present significant fouling problems. The Australian coal is expected to show slagging behavior much more severe than the baseline coal except at very high furnace temperatures. However, the baseline coal is predicted to exhibit opacity problems, as well as having a higher potential for problematic calcium sulfate based low-temperature fouling. These results are in qualitative agreement with the field observations detailed in Appendix C.

The baseline coal has a somewhat higher reactivity than the Australian coal, which is consistent with both the lower average activation energy for the baseline coal and the greater carbon conversion at a given temperature and residence time. The activation energy of the baseline coal at 20.9% and 10.5% oxygen shows some effect of oxygen on the activation energy, with E_a increasing at the lower concentration, may be due to the scatter in the baseline coal kinetic values at the higher oxygen level tested.

RECOMMENDATIONS

High fly ash unburned carbon (UBC) problems are being experienced in some boilers of Union Fenosa's Power Stations. The problem is acute when firing foreign coals of distinct physical and chemical characteristics than the design national coal. Slagging and fouling of the boilers are also operational concerns but not as severe as problems compared to UBC. These boilers are of a Foster Wheeler design using an arch- (or down-) fired furnace. The firing configuration of these units includes a multiburner arrangement fed by Foster Wheeler ball mill pulverizers. Primary air from an air preheater is mixed with coal inside the ball mills, passes through a classifier at the exit of the mill, and then goes to the burners. Preheated secondary air enters the furnace through ports located on the walls below the arch. Surrounding the burner mouth, tertiary air is added through an annular opening. Dampers located in the windbox control the secondary and tertiary air split. Fuel-dependent burner primary, secondary, and tertiary air adjustment are critical at maintaining good combustion in the furnace over the range of fire fuels, which would preclude high fly ash UBC and

high flue gas temperature (related to slagging) problems. Adjustment to the pulverizers, under different fuel scenarios, is also important to improve the combustion condition in these units.

The objectives of this project were set at identifying the root causes of excessive fly ash carbon loss at one boiler and to provide potential, cost-effective solutions while keeping furnace slagging under control. A phased approach was proposed for the project. Phase 1 involved the identification of the root causes of fly ash carbon loss at one boiler. La Robla Station Unit 1 in Leon, Spain, was targeted for this project. Based on the results of work in Phase I, potential solutions will be implemented with the support of field tests. Recommendations will be given for related maintenance work/modifications and additional permanent instrumentation, if required. Furnace control settings will be adjusted depending on the characteristics of the coal being burned to mitigate the high fly ash UBC problem and increase unit thermal performance while keeping furnace slagging under control, as well as avoiding an increase in stack pollutant emissions.

Proposed Phase II Scope

Task 1 – Unit Instrumentation

Prior to Phase II field testing, recommendations will be made for additional instrumentation to help monitor fly ash carbon loss, flue gas temperatures, and burner stoichiometry. Examples of possible instrumentation include CEGRIT ash samplers, a gas sampling grid in the convective pass, optical pyrometers for on-line FEGT monitoring, and on-line flame spectroscopy. An option is to procure the recommended instrumentation on a trial basis for the duration of the testing for Task 2. Data from these instrumentation and regular plant performance data would establish the impact of changes in boiler control settings on fly ash UBC, furnace temperature, and slagging.

Task 2 – Field Testing

The scope of the field testing to be performed in this task is defined from the results of Phase I. Recommended testing will include selective coal pipe dirty-air flow, coal fineness tests, and boiler control parametric tests at full-load conditions for the national coal and two additional foreign coals that were found to be more problematic from the Phase I data analysis. Arrangements will be made for the unit to be off grid-generation and firing the appropriate fuels.

During the field testing, means of increasing carbon burnout will be investigated by adjusting boiler control settings for each of the three fuels. The following activities will be undertaken: 1) balancing O₂ across the furnace by adjustment of burner secondary air dampers may help increase carbon burnout; 2) parametric testing of excess air, secondary/tertiary air split, cyclone rod and vent damper, mill biasing, and primary air; and 3) characterization of waterwall sootblowing practices for slagging/fouling control. During all tests the boiler will be monitored for excessive fouling/slagging. Samples will be taken during each test to determine the effect new burner settings will have on fouling/slagging.

Task 3 – Data Analysis

Data will be analyzed in terms of modifications to boiler control settings and curves to accommodate the unit to better fire the problem fuels. Laboratory results obtained in Phase I will be factored into the data analysis in this task. Slag samples collected in Task 2 will be analyzed with advanced SEM techniques, x-ray fluorescence, and x-ray diffraction to determine the conditions that caused their formation.

Task 4 – Data Analysis and Final Report

The data obtained in the above Tasks will be analyzed. A final report will be issued summarizing the results of the field tests. Guidelines will be given for increasing combustion efficiency while maintaining a manageable degree of furnace slagging.

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APPENDIX A

CCSEM ANALYSES

CCSEM Analysis of Australian Coal

Mineral Fraction, % 9.001

Mineral	Size range, μm						Total	Total % Excluded:
	1.0–2.2	2.2–4.6	4.6–10	10–22	22–46	46–100		
Quartz	1	2.0	1.7	1.8	1.0	1.3	8.9	26.7
Iron Oxide	0.1	0.2	0.4	1.1	1.4	5.2	8.4	76.8
Periclase	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.1	0.6	0.2	0.3	0.3	0.3	1.6	27.2
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Calcite	0.1	0.4	0.2	0.2	1.0	9.1	11.0	76.3
Dolomite	0	0.1	0.1	0.3	0.1	0.5	1.2	47.3
Ankerite	0.0	0.0	0.0	0.1	0.1	0.7	1.0	95.6
Kaolinite	0.6	1.9	1.8	1.5	0.9	2.3	9.0	33.0
Montmorillonite	0.8	2.1	1.5	1.5	0.9	1.3	8.1	23.7
Potassium Aluminosilicate	0.7	0.6	0.8	1.9	1.2	5.1	10.4	55.1
Iron Aluminosilicate	2.7	5.7	4.2	3.9	1.1	0.9	18.5	14.9
Calcium Aluminosilicate	0.0	0.1	0.0	0.0	0.0	0.0	0.2	0.0
Sodium Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.2	0.3	58.4
Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.1	0.2	47.2
Mixed Aluminosilicate	0.1	0.1	0.1	0.1	0.1	0.2	0.7	32.7
Iron Silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcium Silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Calcium Aluminate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrrhotite	0.1	0.0	0.2	0.8	0.4	2.4	3.9	73.4
Oxidized Pyrrhotite	0.0	0.0	0.1	0.2	0.1	0.1	0.5	92.1
Gypsum	0	0.1	0.0	0.0	0.0	0.0	0.1	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	0.5	1.4	1.0	0.6	0.2	0.0	3.8	11.8
Calcium-Aluminum Phosphate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Potassium Chloride	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.1	59.6
Silica-Rich	0.3	0.2	0.2	0.1	0.2	0.7	1.7	42.4
Calcium-Rich	0.1	0.0	0.0	0.0	0.0	0.1	0.2	63.1
Calcium-Silica-Rich	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	1.6	2.5	1.6	1.3	0.9	2.3	10.2	29.1
Totals	9	18.1	14.1	15.8	10.0	33.0	100.0	

% Excluded by Size

Mineral	Size range, μm					
	1.0–2.2	2.2–4.6	4.6–10	10–22	22–46	46–100
Quartz	0	5.1	10.6	35.5	44.7	74.5
Iron Oxide	0.0	41.3	55.7	53.0	56.5	92.0
Periclase	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.0	0.0	0.0	0.0	73.8	100.0
Alumina	0	0.0	0.0	0.0	0.0	0.0
Calcite	20.3	21.8	27.7	54.2	75.8	80.6
Dolomite	0.0	30.1	44.9	0.0	58.9	77.5
Ankerite	0.0	0.0	0.0	100.0	68.6	100.0
Kaolinite	2.9	2.7	19.9	35.0	48.0	69.3
Montmorillonite	0.0	7.0	7.0	15.0	38.4	82.9
Potassium Aluminosilicate	1.8	13.7	19.1	50.8	57.0	74.5
Iron Aluminosilicate	0.6	4.0	11.0	22.5	41.7	82.6
Calcium Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0
Sodium Aluminosilicate	0.0	0.0	100.0	0.0	80.1	69.6
Aluminosilicate	0.0	0.0	0.0	0.0	73.9	100.0
Mixed Aluminosilicate	0.0	0.0	0.0	0.0	57.8	64.7
Iron Silicate	0.0	0.0	0.0	0.0	0.0	0.0
Calcium Silicate	0.0	0.0	100.0	0.0	0.0	0.0
Calcium Aluminate	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.0	0.0	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.0	81.5	66.6	81.5	76.6
Oxidized Pyrrhotite	0.0	0.0	78.4	100.0	83.6	100.0
Gypsum	0.0	0.0	0.0	0.0	0.0	0.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	0.0	11.1	13.3	6.4	40.5	100.0
Calcium-Aluminum Phosphate	0.0	0.0	0.0	0.0	0.0	0.0
Potassium Chloride	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Barite	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Aluminosilicate	0.0	0.0	0.0	0.0	0.0	100.0
Silica-Rich	0.0	0.0	12.9	0.0	61.3	84.8
Calcium-Rich	0	0.0	66.0	0.0	0.0	100.0
Calcium-Silica-Rich	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	2.5	2.6	19.6	27.6	56.9	73.7

CCSEM Analysis of Baseline Coal

Mineral Fraction, %

39.239

Mineral	Size range, μm						Total	Total % Excluded:
	1.0–2.2	2.2–4.6	4.6–10	10–22	22–46	46–100		
Quartz	0.1	0.3	0.3	0.1	0.3	2.1	3.2	96.1
Iron Oxide	0.0	0.0	0.2	0.6	1.1	0.3	2.3	78.7
Periclase	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	0.0	0.0	0.0	0.0	0.0	0.0	0.0	72.3
Alumina	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Calcite	0.1	0.5	0.9	1.0	0.8	3.5	6.8	90.3
Dolomite	0.0	0.0	0.0	0.1	0.0	0.0	0.1	66.0
Ankerite	0.1	0.4	0.8	0.6	0.6	3.9	6.4	88.4
Kaolinite	0.4	0.4	0.5	0.2	0.4	1.5	3.4	79.4
Montmorillonite	0.1	0.2	0.1	0.4	0.2	1.0	2.0	95.3
Potassium Aluminosilicate	0.4	0.9	1.4	1.3	1.7	11.1	16.8	89.4
Iron Aluminosilicate	0.1	0.1	0.1	0.1	0.0	0.0	0.4	99.4
Calcium Aluminosilicate	0.0	0.1	0.0	0.1	0.1	0.1	0.4	87.9
Sodium Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Aluminosilicate	0.0	0.0	0.0	0.0	0.0	0.5	0.5	100.0
Mixed Aluminosilicate	0.1	0.2	0.1	0.2	0.1	1.7	2.5	94.7
Iron Silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Calcium Silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.1	100.0
Calcium Aluminate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.1	0.3	0.5	0.6	0.3	0.9	2.6	83.5
Pyrrhotite	1.4	1.9	3.6	5.3	2.6	9.2	24.0	72.6
Oxidized Pyrrhotite	0.0	0.0	0.1	0.1	0.1	0.1	0.3	93.4
Gypsum	0.1	0.0	0.1	0.1	0.1	0.2	0.5	94.9
Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	0	0.1	0.1	0.1	0.1	0.0	0.5	58.8
Calcium-Aluminum Phosphate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Potassium Chloride	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Barite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Aluminosilicate	0.2	0.1	0.1	0.0	0.2	0.2	0.7	74.7
Silica-Rich	0.0	0.1	0.0	0.0	0.1	0.1	0.4	92.6
Calcium-Rich	0.1	0.1	0.1	0.0	0.1	0.2	0.5	82.7
Calcium-Silica-Rich	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	2.1	2.1	2.3	2.5	3.3	13.1	25.3	77.7
Totals	5.6	8.0	11.6	13.3	12.0	49.5	100.0	

% Excluded by Size

Mineral	Size range, μm					
	1.0–2.2	2.2–4.6	4.6–10	10–22	22–46	46–100
Quartz	85.9	79.4	91.0	100.0	93.0	100.0
Iron Oxide	100.0	100.0	62.7	88.0	70.6	100.0
Periclase	0.0	0.0	0.0	0.0	0.0	0.0
Rutile	100.0	0.0	58.4	0.0	0.0	0.0
Alumina	0.0	0.0	0.0	0.0	0.0	0.0
Calcite	92.5	100.0	96.0	97.5	90.6	85.5
Dolomite	100	0.0	85.3	45.2	77.7	0.0
Ankerite	75.0	82.2	67.5	64.6	70.9	100.0
Kaolinite	31.5	43.8	74.7	100.0	88.0	100.0
Montmorillonite	46.8	93.8	93.8	100.0	97.3	100.0
Potassium Aluminosilicate	67.3	84.8	87.6	91.7	93.9	90.0
Iron Aluminosilicate	95.7	100.0	100.0	100.0	100.0	100.0
Calcium Aluminosilicate	100.0	64.0	100.0	100.0	100.0	100.0
Sodium Aluminosilicate	0.0	0.0	0.0	0.0	100.0	0.0
Aluminosilicate	0.0	0.0	0.0	0.0	0.0	100.0
Mixed Aluminosilicate	84.1	79.9	67.2	100.0	84.6	100.0
Iron Silicate	100.0	0.0	0.0	0.0	0.0	0.0
Calcium Silicate	0.0	100.0	100.0	0.0	0.0	100.0
Calcium Aluminate	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	69.6	64.8	88.6	67.5	78.3	100.0
Pyrrhotite	46.1	71.6	71.4	86.0	87.3	65.4
Oxidized Pyrrhotite	100.0	0.0	100.0	100.0	78.5	100.0
Gypsum	90.0	51.9	100.0	100.0	87.2	100.0
Barite	0.0	0.0	0.0	0.0	0.0	0.0
Apatite	36.1	100.0	61.9	0.0	89.8	0.0
Calcium-Aluminum Phosphate	0.0	0.0	0.0	0.0	0.0	0.0
Potassium Chloride	0	0.0	0.0	0.0	0.0	0.0
Gypsum-Barite	0.0	0.0	0.0	0.0	0.0	0.0
Gypsum-Aluminosilicate	38.8	35.8	91.9	0.0	92.9	100.0
Silica-Rich	82.9	89.7	100.0	0.0	79.4	100.0
Calcium-Rich	68.5	42.8	100.0	100.0	67.3	100.0
Calcium-Silica-Rich	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	49.2	63.1	72.3	82.6	88.8	81.9

APPENDIX B

FACT COAL LIQUID PHASES

T, °C	Baseline Coal		Baseline Coal		Baseline Coal		Baseline Coal		Baseline Coal		Baseline Coal		Baseline Coal		Baseline Coal		Baseline Coal	
	Liquids, wt%	Australian Coal Liquids, wt%	Viscosity, Log ₁₀ poise	Viscosity, Log ₁₀ poise	Australian Coal Viscosity, Log ₁₀ poise	Deposition Rate, g deposit/kg ash fed	Deposition Rate, g deposit/kg ash fed	Australian Coal Deposition Rate, g deposit/kg ash fed	Solid Sulfates, wt%	Solid Sulfates, wt%	Australian Coal	Solid Sulfates, wt%	Australian Coal	Solid Sulfates, wt%	Australian Coal	Solid Sulfates, wt%	Australian Coal	Solid Sulfates, wt%
1500	76	77	1.91	2.60	2.60	103	76	76	0	0								
1475	61	75	2.05	2.74	2.74	76	70	70	0	0								
1450	50	74	2.21	2.88	2.88	57	65	65	0	0								
1425	43	74	2.37	3.09	3.09	45	61	61	0	0								
1400	38	72	2.53	3.33	3.33	36	55	55	0	0								
1375	34	70	2.69	3.56	3.56	30	49	49	0	0								
1350	31	68	2.85	3.81	3.81	26	44	44	0	0								
1325	29	62	3.02	3.96	3.96	22	39	39	0	0								
1300	27	62	3.18	4.14	4.14	19	36	36	0	0								
1275	24	61	3.38	4.32	4.32	16	34	34	0	0								
1250	19	60	3.68	4.54	4.54	11	32	32	0	0								
1225	16	53	3.81	4.70	4.70	8	27	27	0	0								
1200	13	43	3.81	4.97	4.97	5	19	19	0	0								
1175	11	36	3.82	5.29	5.29	4	14	14	0	0								
1150	7	31	4.19	5.58	5.58	1	11	11	0	0								
1125	5	28	4.65	5.87	5.87	0	9	9	0	0								
1100	4	26	5.03	6.14	6.14	0	8	8	0	0								
1075	4	24	5.38	6.42	6.42	0	6	6	0	0								
1050	3	22	5.70	6.69	6.69	0	5	5	0	0								
1025	3	21	6.02	6.97	6.97	0	4	4	0	0								
1000	3	20	6.34	7.25	7.25	0	4	4	0	0								
975	3	19	6.66	7.53	7.53	0	3	3	0	0								
950	2	18	6.98	7.81	7.81	0	2	2	0	0								
925	2	0	7.29	NA	NA	0	0	0	0	0								
900	0	0	NA	NA	NA	0	0	0	0	0								
875	0	0	NA	NA	NA	0	0	0	0	0								
850	0	0	NA	NA	NA	0	0	0	0	0								
825	0	0	NA	NA	NA	0	0	0	3	3								
800	0	0	NA	NA	NA	0	0	0	3	3								
775	0	0	NA	NA	NA	0	0	0	24	24								
750	0	0	NA	NA	NA	0	0	0	25	25								
725	0	0	NA	NA	NA	0	0	0	27	27								
700	0	0	NA	NA	NA	0	0	0	27	27								
675	0	0	NA	NA	NA	0	0	0	28	28								
650	0	0	NA	NA	NA	0	0	0	28	28								
625	0	0	NA	NA	NA	0	0	0	31	31								
600	0	0	NA	NA	NA	0	0	0	33	33								
575	0	0	NA	NA	NA	0	0	0	33	33								
550	NA	0	NA	NA	NA	0	0	0	NA	NA								
525	NA	0	NA	NA	NA	0	0	0	NA	NA								
500	NA	0	NA	NA	NA	0	0	0	NA	NA								

APPENDIX C

EVALUATION OF UNBURNED CARBON AND SLAGGING PROBLEMS AT UNION FENOSA LA ROBLA I POWER PLANT

EVALUATION OF UNBURNED CARBON AND SLAGGING PROBLEMS AT UNION FENOSA LA ROBLA I POWER PLANT

Final Report

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EVALUATION OF UNBURNED CARBON AND SLAGGING PROBLEMS AT UNION FENOSA LA ROBLA I POWER PLANT

INTRODUCTION

The University of North Dakota Energy & Environmental Research Center (EERC) and the Lehigh University Energy Research Center (LUERC) undertook a site visit to collect information that would be used to assess slagging and unburned carbon problems at Union Fenosa's La Robla I Power Station.

La Robla I is a 270-MW Foster Wheeler arch-fired system. The unit is located at the mine that provides a portion of the semianthracite coal. The remaining coals used at La Robla I are foreign coals from South Africa, Russia, Australia, and China. The challenges at the La Robla I station stem from the varied supply of fuels, which are different from the design coal.

This report covers the analysis of the specific slagging problem and provides remediation measures to help limit the amount of slagging at the station. Another report provided by LUERC will cover the unburned carbon problems and unit operation. A future report covering all aspects of the project, including the carbon conversion kinetics and drop-tube furnace testing, will be issued in February 2003.

ANALYTICAL RESULTS AND DISCUSSION

La Robla Coal

A sample of the La Robla coal was submitted for proximate–ultimate analyses, x-ray fluorescence (XRF), and computer-controlled scanning electron microscopy (CCSEM). The proximate–ultimate analyses are measures of the coal properties, while XRF shows the bulk chemical composition of the mineral matter when the coal has been ashed at 750°C. CCSEM is an analysis of the size, shape, chemistry, and location of the mineral matter in the coal.

Table 1 presents the proximate analysis, and Table 2 shows the ultimate analysis for the La Robla I coal as received and as determined. The detailed results can be found in Appendix A.

Table 1. Proximate Results for the La Robla Coal

	As Determined	As Received
Moisture, %	1.09	12.5
Volatile Matter, %	13.68	12.10
Fixed Carbon, %	77.53	68.59
Ash, %	7.71	6.81

Table 2. Ultimate Analyses for the La Robla Coal

	As Determined	As Received
Hydrogen, %	3.11	4.03
Carbon, %	73.02	64.57
Nitrogen, %	1.62	1.43
Sulfur, %	2.13	1.88
Oxygen, %	12.42	21.27
Ash, %	7.71	6.81

The bulk chemical composition of the mineral matter contained in the coal was determined by XRF. For quality control purposes, samples are periodically run twice, which was the case for the La Robla I coal sample. Table 3 presents the XRF results for both analyses of the same ash sample. The results are reported in Table 3 as elemental weight percent (wt%) and oxide wt%; normalization and renormalization on a sulfur-free basis can be found in Appendix B.

The chemical composition of the inorganic matter in the coal is primarily silicon, aluminum, iron, and calcium. Sulfur is significant in the bulk chemical composition determined by XRF but was found only in minor amounts on the deposits and slags as a result of the temperatures at which the deposits and slags were formed. The ultimate and CCSEM analyses show that most of the sulfur and iron are derived from iron sulfide minerals such as pyrite.

Table 3. XRF Results of the La Robla I Baseline Coal Sample

	Si	Al	Fe	Ti	P	Ca	Mg	Na	K	S
La Robla Coal	31.1	22.5	15.7	0.8	0.8	15.1	1.8	0.2	2.8	9.1
Duplicate Sample	30.9	22.1	15.8	0.8	0.8	15.4	1.8	0.2	2.8	9.3

A CCSEM analysis was performed on the La Robla I coal sample to determine the mineral phases contributing to the formation of the ash deposits and slag. A summary report of the CCSEM analysis can be found in Appendix C. Table 4 shows the main phases and their wt% on a mineral basis. For the table, five primarily aluminosilicate phases were combined. The average composition of the unclassified particles roughly parallels the bulk chemical composition, with the exception of sulfur.

Table 4. CCSEM Results of the La Robla I Baseline Coal Sample

Phase	Quartz	Iron Oxide	Calcite	Aluminosilicate	Iron Sulfide	Unclassified
Mineral, wt%	3.2	2.3	6.8	31.1	26.9	25.3

The summary report in Appendix C shows that the mineral content is very high at 39% by weight on a coal basis. This discrepancy with the proximate–ultimate analysis can be explained by several large particles encountered. Nearly 50% of the mineral matter was found to be in the

46–100- μm range, which consisted primarily of iron sulfide and potassium-rich aluminosilicate such as potassium feldspar or a clay mineral derived from the feldspar.

Deposit and Slag Analyses

Deposit and slag samples were collected from six different locations in the boiler. The locations were roughly the corners of the boiler sampled at different levels. These samples represent a baseline deposit and slag, the deposit/slag collected during an increased-oxygen test, a second baseline test, and a burner vein rod test. General observations from the samples indicate that the aluminosilicate phases contained in the coal came to a complete melt. The iron sulfides are dissociated into their component parts, with sulfur volatilized and generally absent in the deposits. The remaining iron is largely immiscible with the aluminosilicate melt and remains as discrete grains, but iron is present in the glassy matrix as well. Iron can enter the melt by exsolution from an otherwise immiscible iron phase at temperatures starting at about 1350°C. The relative temperatures can be inferred from the iron content in the matrix or glassy phase, with higher iron contents coming from hotter zones. The presence of the plagioclase feldspar mineral anorthite indicates that temperatures were in excess of 1500°C, the lowest temperature at which anorthite will crystallize from a melt. As anorthite crystallizes, only trace to minor amounts of iron and potassium can be incorporated into the crystalline structure, and the liquid phase from which the anorthite is crystallizing becomes enriched in those elements at the edges of the crystals.

Baseline Test

The first baseline and the oxygen test samples were collected from five different locations. These locations were as follows:

- NE Level 2
- SW Level 1.5
- NW Level 1.5
- SE Level 2
- NE Level 1.5

Table 5 summarizes a few of the selected analyses to represent the matrix or glassy portion of the sample.

The higher iron contents are from areas where the heat was much higher and iron was incorporated into the melt. Figure 1 is an SEM image that indicates high temperature. The bright white areas are the iron-rich grains and the darker gray laths are plagioclase feldspar crystals of anorthite. The medium gray is the matrix, or the amorphous portion, of the sample. There are small white rims, or overgrowths, around the anorthite crystals that are the result of iron not being incorporated into the anorthite crystal except in small amounts. The iron is “pushed” away from the crystal and ends up being concentrated in the amorphous matrix around the crystal. Potassium behaves in a similar manner with anorthite crystallization.

Table 5. Elemental Analysis of the Amorphous Portion of the Baseline Deposit, wt%

	NE Level 2	NE Level 2	SW Level 1.5	NW Level 1.5	SE Level 2	NE Level 1.5	NE Level 1.5
Na	0.19	0.2	0.07	0.11	0.26	0.4	0.09
Mg	2.49	2.5	1.98	2.41	3.01	2.18	2.22
Al	14.38	14.11	13.99	12.37	13.7	8.39	8.59
Si	44.25	44.72	32.85	34.63	53.26	32.99	32.48
P	1.49	1.28	0.66	0.96	1.95	1.98	1.73
S	0	0	0.11	0.17	0	0.09	0
Cl	0	0.21	0.04	0.02	0.19	0	0
K	8.14	7.99	4.53	6.05	12.36	3.56	2.88
Ca	12.78	13.11	17.95	22.33	6.62	30.36	29.91
Ti	0.86	0.88	1.21	1.89	0.23	1.32	0.2
Cr	0	0.11	0.1	0.54	0	0.03	0.33
Fe	15.43	14.9	25.98	18.51	6.76	17.76	19.31
Ba	0	0	0.53	0	1.65	0.95	2.26

Figure 1. SEM image of the sample taken from the SW Level 1.5 sampling port. This represents a high-temperature sample.

Figure 2 is an SEM image of the sample taken from the SE Level 2 sampling port representing a cooler sample. The iron-bearing grains are blocklike in appearance; there is still some porosity, showing that the sample did not come to a complete liquid melt. The smaller iron-rich grains have not been incorporated into the melt, giving the matrix material a darker gray appearance using backscattered imaging techniques. Table 5 shows the iron content for the matrix of Figure 1 to be 26 wt% and the iron content of the matrix material from Figure 2 to be 6.8 wt%. The anorthite and iron-rich grains have consistent chemistries that are not temperature-dependent. Chemical analyses of these phases can be seen in Appendix D.

Oxygen Test

The SEM morphologies of the oxygen test samples show that these were all of a similar temperature, with the possible exception of the sample taken from NE Level 1.5. This sample appeared to have not come to complete melt. Table 6 is a summary of the matrix portion from the oxygen test samples. This sample is similar to the baseline samples; there is a direct correlation between iron content and temperature.

The NE Level 1.5 and SE Level 2 samples appear to have formed in slightly cooler environments as compared to the other samples. The NE Level 1.5 sample from the baseline test showed complete melt, while this location was the coolest of the samples taken during the O₂ test. The SE Level 2 sample from the O₂ test was moderately hot, and the coolest came from the baseline test. More chemical analyses of the O₂ test samples can be seen in Appendix D.

Figure 2. SEM image of the sample taken from the SE Level 2 sampling port. This sample was formed at a lower temperature than the sample shown in Figure 1.

Table 6. Elemental Analysis of the Amorphous Portion of the O₂ Test Deposit, wt%

	NE Level 2	NW Level 1.5	NE Level 1.5	SE Level 2	SW Level 1.5
Na	0.22	0.19	0.58	0	0.39
Mg	1.75	2.12	3.25	3.21	2.72
Al	14.33	12.51	13.18	10.75	10
Si	38.21	31.7	43.7	36.13	37.44
P	1.04	0.7	1.27	1.47	0.8
S	0	0	0	0	0
Cl	0.05	0	0	0.28	0.17
K	6.39	3.9	7.38	4.38	4.96
Ca	14.9	20.85	16.32	23.93	22.48
Ti	1.45	0.56	1.75	1.1	0.85
Cr	0.22	0	0.03	0.38	0.11
Fe	21.43	26.23	12.31	18.16	19.11
Ba	0	1.24	0.22	0.22	0.96

Figures 3 and 4 represent the hottest and coolest zones from the O₂ test samples. Figure 3 is from the NW Level 1.5 sample showing an iron-rich matrix, well-developed anorthite, and iron particles growing from coalescing smaller particles crystallizing from the melt. Figure 4 represents the NE Level 1.5 sample where there was more porosity, poorly developed anorthite, and not as much iron dispersed into the matrix.

Figure 3. SEM image of the NW Level 1.5 sample showing complete melt and recrystallization.

Figure 4. SEM image of the NE Level 1.5 sample showing that temperatures were not high enough to reach a complete melt.

Baseline 2 Test

A second set of baseline samples was collected on the day following the first baseline sampling and the O₂ test. Three locations were sampled, and all showed similar results, with the SW Level 1.5 sample showing the lowest temperatures and the SE Level 2 sample showing the highest temperatures. Chemical analyses can be seen in Appendix D. Table 7 represents the matrix material from the second baseline test.

Burner Vein Test

Three locations were sampled in a burner vein test. NW Level 1.5 was sampled rather than NW Level 2, which was sampled in the second baseline test. The other locations remained the same. Areas not sampled mean there was no sample to collect in those locations. Table 8 shows the chemical analyses of the matrix material from the burner vein samples. All show a high degree of melting and recrystallization. Further chemical analyses can be found in Appendix D.

Table 7. Elemental Analysis of the Amorphous Portion of the Second Baseline Test Deposit, wt%

	SE Level 2	SE Level 2	NW Level 2	NW Level 2	SW Level 1.5	SW Level 1.5
Na	0.12	0	0.37	0.06	0.56	0
Mg	3.43	3.15	3.82	3.05	0.27	0.49
Al	5.77	8.27	9.9	10.07	22.63	24.5
Si	32.56	31.33	35.71	36.32	35.58	35.23
P	2.19	1.3	1.54	1.81	0.1	0.02
S	0	0	0.15	0.42	0	0
Cl	0	0.13	0.1	0	0	0.06
K	2.8	2.98	7.15	7.1	1.7	1.99
Ca	30.08	28.32	21.37	23.39	27.9	20.92
Ti	1.22	3.04	0.27	1.04	0.56	0.83
Cr	0	0	0.22	0.27	0.48	0
Fe	20.99	21.48	18.07	15.57	10.21	15.96
Ba	0.85	0	1.33	0.91	0	0

Table 8. Elemental Analysis of the Amorphous Portion of the Burner Vein Test Deposit, wt%

	NW Level 2	NW Level 2	SE Level 2	SE Level 2	NW Level 1.5	NW Level 1.5
Na	0	0	0.18	0.29	0.26	0.14
Mg	2.91	2.38	2.93	2.59	2.56	2.8
Al	12.37	12.31	11.07	10.58	11.65	10.33
Si	36.98	36.44	35.11	37.36	30.75	31.65
P	1.29	0.72	1.3	0.93	1.28	1.18
S	0	0	0.05	0	0.08	0.09
Cl	0.04	0	0.03	0.03	0.36	0.32
K	5.8	6.36	6.75	7.26	3.37	4.52
Ca	19.65	17.57	23.03	22.81	23.87	24.87
Ti	0	1.28	1.59	1.58	0.82	1.31
Cr	0.35	0.57	0	0.34	0.1	0
Fe	20.61	22.38	17.37	16.22	22.88	22.78
Ba	0	0	0.57	0	2.03	0

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The presence of anorthite crystals in the bulk of the deposits indicates that the temperatures were in excess of 1350°C. This observation is consistent with the temperatures gathered with the optical pyrometer during the sampling period. The field notes and temperatures can be found in Appendix E. More discussion on this topic will follow in the final report to be issued in February.

The bulk of the slagging problems are most likely linked to the same operational parameters driving the unburned-carbon problems. The slagging in almost all cases was due to elevated temperatures, not specific fuel chemistries. The most severe slagging occurred when the

temperature at the sampling port was in excess of 1500°C. Problems with slagging were first observed when temperatures started exceeding 1350°C.

Elevated temperatures and “hot spots” are likely caused by some of the same issues referred to in the report by LUERC. Poor mill performance and a poor distribution of the coal from the mills to the specific burners cause elevated temperatures in the regions where the slag samples were extracted. The biasing of the mills may be caused by the maintenance condition of the mills.

The second cause of the hot areas would be poor combustion air mixing and heating. Poor combustion mixing leads to oxygen stratification and, therefore, increased temperatures in certain areas. Air preheater plugging was observed and reduces the temperature of the air in the windbox. Reduced temperature in the windbox leads to poor combustion conditions, resulting in slagging and unburned carbon.

Phase II of the project should focus on the implementation of the maintenance problems pointed out in the report issued by LUERC. When some of the maintenance issues are addressed, more parametric testing can be completed by Union Fenosa staff under the guidance of EERC and LUERC personnel. The ability to more effectively change operating parameters will help greatly in better determining the cause of the slagging and unburned-carbon problems.

APPENDIX A

PROXIMATE–ULTIMATE ANALYSES OF THE LA ROBLA I COAL

Coal Analysis Report

Table A-1. Proximate Analysis for the La Robla I Baseline Coal

Air Dry Loss:	11.57%			
	As Det., %	As Recd., %	Moist. Free, %	Moist. Ash Free%
Moisture	1.09	12.50	NA	NA
Volatile Matter	13.68	12.10	13.83	15.00
Fixed Carbon (Ind.)	77.53	68.59	78.38	85.00
Ash	7.71	6.81	7.79	N/A

Table A-2. Ultimate Analysis for the La Robla I Baseline Coal

Air Dry Loss:	11.57%			
	As Det., %	As Recd., %	Moist. Free, %	Moist Ash Free%
Hydrogen	3.11	4.03	3.02	3.28
Carbon	73.02	64.57	73.82	80.06
Nitrogen	1.62	1.43	1.64	1.78
Sulfur	2.13	1.88	2.15	2.33
Oxygen (Ind.)	12.42	21.27	11.58	12.56
Ash	7.71	6.81	7.79	NA
Heating Value, Btu/lb	0	0	0	0
Calc. Calorific Value	11759	10398		

As-received hydrogen not including hydrogen from moisture: 2.64%

As-received oxygen not including oxygen from moisture: 10.13%

APPENDIX B

BULK CHEMICAL COMPOSITION BY XRF OF THE LA ROBLA I BASELINE COAL

Table B-1. Bulk Chemical Composition by XRF of the La Robla I Baseline Coal

Oxides, wt%	A	B	C	Elemental, wt%	D	E
SiO ₂	35.9	36.0	41.0	Si	31.1	34.3
Al ₂ O ₃	22.9	22.9	26.1	Al	22.5	24.7
Fe ₂ O ₃	12.1	12.1	13.8	Fe	15.7	17.3
TiO ₂	0.73	0.73	0.83	Ti	0.8	0.9
P ₂ O ₅	1.03	1.03	1.18	P	0.8	0.9
CaO	11.4	11.4	13.0	Ca	15.1	16.6
MgO	1.59	1.60	1.82	Mg	1.8	2.0
Na ₂ O	0.18	0.18	0.20	Na	0.2	0.3
K ₂ O	1.80	1.80	2.1	K	2.8	3.0
SO ₃	12.2	12.2	–	S	9.1	–
Total	99.8					

A – Oxide concentrations (wt%) on an ash basis.

B – Oxide concentrations normalized to a closure of 100%.

C – Oxide concentrations renormalized to an SO₃–free basis.

D – Elemental concentrations (wt%) on an ash basis.

E – Elemental concentrations renormalized to a S-free basis

Table B-2. Duplicate Sample Results

Oxides, wt%	A	B	C	Elemental, wt%	D	E
SiO ₂	35.7	35.7	40.9	Si	30.9	34.1
Al ₂ O ₃	22.5	22.6	25.8	Al	22.1	24.4
Fe ₂ O ₃	12.2	12.2	14.0	Fe	15.8	17.4
TiO ₂	0.73	0.73	0.83	Ti	0.8	0.9
P ₂ O ₅	1.03	1.03	1.18	P	0.8	0.9
CaO	11.6	11.6	13.3	Ca	15.4	17.0
MgO	1.60	1.60	1.83	Mg	1.8	2.0
Na ₂ O	0.16	0.16	0.18	Na	0.2	0.2
K ₂ O	1.80	1.80	2.10	K	2.80	3.10
SO ₃	12.6	12.6	–	S	9.3	–
Total	99.9					

A – Oxide concentrations (wt%) on an ash basis.

B – Oxide concentrations normalized to a closure of 100%.

C – Oxide concentrations renormalized to an SO₃–free basis.

D – Elemental concentrations (wt%) on an ash basis.

E – Elemental concentrations renormalized to a S-free basis.

APPENDIX C

CCSEM RESULTS FOR LA ROBLA I BASELINE COAL

SAMPLE DESCRIPTION ---> La Robla I Baseline Coal

SUMMARY OF PARAMETERS

PERCENT EPOXY USED	=	50.8
TOTAL MINERAL AREA ANALYZED AT 800.0 MAG	=	3786.3
NORMALIZED AREA ANALYZED AT 800.0 MAG	=	751846.0
MINERAL AREA ANALYZED 250.0 MAG	=	70823.4
NORMALIZED AREA ANALYZED 250.0 MAG	=	1262262.0
TOTAL MINERAL AREA ANALYZED AT 50.0 MAG	=	3480962.0
NUMBER OF FRAMES AT 800.0 MAG	=	15
NUMBER OF FRAMES AT 250.0 MAG	=	17
NUMBER OF FRAMES AT 50.0 MAG	=	12
TOTAL MINERAL WGT % ON A COAL BASIS	=	39.239
TOTAL NUMBER OF POINTS ANALYZED	=	3600
NUMBER OF POINTS UNDER THRESHOLD	=	201

WEIGHT PERCENT ON A MINERAL BASIS

	1.0 TO 2.2	2.2 TO 4.6	4.6 TO 10.0	10.0 TO 22.0	22.0 TO 46.0	46.0 TO 100.0	TOTALS	% EXCLUDED
QUARTZ	.1	.3	.3	.1	.3	2.1	3.2	96.1
IRON OXIDE	.0	.0	.2	.6	1.1	.3	2.3	78.7
PERICLASE	.0	.0	.0	.0	.0	.0	.0	.0
RUTILE	.0	.0	.0	.0	.0	.0	.0	72.3
ALUMINA	.0	.0	.0	.0	.0	.0	.0	.0
CALCITE	.1	.5	.9	1.0	.8	3.5	6.8	90.3
DOLOMITE	.0	.0	.0	.1	.0	.0	.1	66.0
ANKERITE	.1	.4	.8	.6	.6	3.9	6.4	88.4
KAOLINITE	.4	.4	.5	.2	.4	1.5	3.4	79.4
MONTMORILLONITE	.1	.2	.1	.4	.2	1.0	2.0	95.3
K AL-SILICATE	.4	.9	1.4	1.3	1.7	11.1	16.8	89.4
FE AL-SILICATE	.1	.1	.1	.1	.0	.0	.4	99.4
CA AL-SILICATE	.0	.1	.0	.1	.1	.1	.4	87.9
NA AL-SILICATE	.0	.0	.0	.0	.0	.0	.0	100.0
ALUMINOSILICATE	.0	.0	.0	.0	.0	.5	.5	100.0
MIXED AL-SILICA	.1	.2	.1	.2	.1	1.7	2.5	94.7
FE SILICATE	.0	.0	.0	.0	.0	.0	.0	100.0
CA SILICATE	.0	.0	.0	.0	.0	.0	.1	100.0
CA ALUMINATE	.0	.0	.0	.0	.0	.0	.0	.0
PYRITE	.1	.3	.5	.6	.3	.9	2.6	83.5
PYRRHOTITE	1.4	1.9	3.6	5.3	2.6	9.2	24.0	72.6
OXIDIZED PYRRHO	.0	.0	.1	.1	.1	.1	.3	93.4
GYPSUM	.1	.0	.1	.1	.1	.2	.5	94.9
BARITE	.0	.0	.0	.0	.0	.0	.0	.0
APATITE	.0	.1	.1	.1	.1	.0	.5	58.8
CA AL-P	.0	.0	.0	.0	.0	.0	.0	.0
KCL	.0	.0	.0	.0	.0	.0	.0	.0
GYPSUM/BARITE	.0	.0	.0	.0	.0	.0	.0	.0
GYPSUM/AL-SILIC	.2	.1	.1	.0	.2	.2	.7	74.7
SI-RICH	.0	.1	.0	.0	.1	.1	.4	92.6
CA-RICH	.1	.1	.1	.0	.1	.2	.5	82.7
CA-SI RICH	.0	.0	.0	.0	.0	.0	.0	.0
UNCLASSIFIED	2.1	2.1	2.3	2.5	3.3	13.1	25.3	77.7
TOTALS	5.6	8.0	11.6	13.3	12.0	49.5	100.0	

SAMPLE DESCRIPTION ---> La Robla I Baseline Coal

Percent excluded as a function of particle size and phase.

	1.0 TO 2.2	2.2 TO 4.6	4.6 TO 10.0	10.0 TO 22.0	22.0 TO 46.0	46.0 TO 100.0

QUARTZ	85.9	79.4	91.0	100.0	93.0	100.0
IRON OXIDE	100.0	100.0	62.7	88.0	70.6	100.0
PERICLASE	.0	.0	.0	.0	.0	.0
RUTILE	100.0	.0	58.4	.0	.0	.0
ALUMINA	.0	.0	.0	.0	.0	.0
CALCITE	92.5	100.0	96.0	97.5	90.6	85.5
DOLOMITE	100.0	.0	85.3	45.2	77.7	.0
ANKERITE	75.0	82.2	67.5	64.6	70.9	100.0
KAOLINITE	31.5	43.8	74.7	100.0	88.0	100.0
MONTMORILLONITE	46.8	93.8	93.8	100.0	97.3	100.0
K AL-SILICATE	67.3	84.8	87.6	91.7	93.9	90.0
FE AL-SILICATE	95.7	100.0	100.0	100.0	100.0	100.0
CA AL-SILICATE	100.0	64.0	100.0	100.0	100.0	100.0
NA AL-SILICATE	.0	.0	.0	.0	100.0	.0
ALUMINOSILICATE	.0	.0	.0	.0	.0	100.0
MIXED AL-SILICA	84.1	79.9	67.2	100.0	84.6	100.0
FE SILICATE	100.0	.0	.0	.0	.0	.0
CA SILICATE	.0	100.0	100.0	.0	.0	100.0
CA ALUMINATE	.0	.0	.0	.0	.0	.0
PYRITE	69.6	64.8	88.6	67.5	78.3	100.0
PYRRHOTITE	46.1	71.6	71.4	86.0	87.3	65.4
OXIDIZED PYRRHO	100.0	.0	100.0	100.0	78.5	100.0
GYPSUM	90.0	51.9	100.0	100.0	87.2	100.0
BARITE	.0	.0	.0	.0	.0	.0
APATITE	36.1	100.0	61.9	.0	89.8	.0
CA AL-P	.0	.0	.0	.0	.0	.0
KCL	.0	.0	.0	.0	.0	.0
GYPSUM/BARITE	.0	.0	.0	.0	.0	.0
GYPSUM/AL-SILIC	38.8	35.8	91.9	.0	92.9	100.0
SI-RICH	82.9	89.7	100.0	.0	79.4	100.0
CA-RICH	68.5	42.8	100.0	100.0	67.3	100.0
CA-SI RICH	.0	.0	.0	.0	.0	.0
UNCLASSIFIED	49.2	63.1	72.3	82.6	88.8	81.9

SAMPLE DESCRIPTION ---> La Robla I Baseline Coal

Average phase composition.

(Percent Relative X-ray Intensity)

	SI	AL	FE	TI	P	CA	MG	NA	K	S	BA	CL
QUARTZ	95.5	1.1	1.0	.2	.3	.3	.1	.1	.2	.4	.2	.7
IRON OXIDE	.5	.4	87.8	.1	.2	6.8	2.0	.6	.2	.7	.2	.5
PERICLASE	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
RUTILE	1.4	1.6	1.1	94.6	.0	.5	.1	.1	.2	.1	.0	.2
ALUMINA	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
CALCITE	.7	.6	2.8	.1	.2	93.2	.3	.2	.2	.6	.4	.7
DOLOMITE	.3	.6	9.8	.2	.1	68.8	16.9	.3	.3	1.6	.4	.6
ANKERITE	1.2	1.2	33.3	.1	.3	48.7	12.0	.3	.3	1.3	.4	.8
KAOLINITE	51.9	37.2	1.6	.4	.4	.6	.3	.2	1.9	3.4	.6	1.3
MONTMORILLONITE	54.1	32.5	2.1	.9	.5	.7	.4	.2	3.4	3.4	.4	1.3
K AL-SILICATE	50.7	30.6	2.7	.8	.4	.7	.7	.4	8.6	2.6	.7	1.2
FE AL-SILICATE	42.7	27.8	17.5	.8	.6	1.4	1.7	.4	2.7	2.0	.7	1.7
CA AL-SILICATE	43.8	27.6	2.6	.5	2.9	14.5	1.2	.1	2.5	2.5	.6	1.2
NA AL-SILICATE	69.2	19.4	.5	.0	.0	.5	.0	9.5	.2	.0	.0	.7
ALUMINOSILICATE	71.4	23.7	.3	.1	.2	.4	.0	.2	2.2	.1	1.1	.4
MIXED AL-SILICA	46.2	29.6	5.0	2.0	1.2	2.7	.9	.4	6.6	2.1	1.2	2.0
FE SILICATE	59.3	3.1	24.8	.0	2.1	.3	1.1	2.5	1.1	1.1	1.1	3.6
CA SILICATE	45.9	1.6	2.0	.0	.7	46.4	.5	.2	.3	.8	.0	1.5
CA ALUMINATE	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
PYRITE	1.1	1.4	31.8	.3	.3	1.8	.6	.4	.3	59.6	.4	2.0
PYRRHOTITE	1.0	.9	46.5	.1	.2	1.1	.3	.3	.2	48.9	.1	.6
OXIDIZED PYRRHO	1.9	1.6	67.8	.2	.3	2.2	1.8	.5	.8	21.3	.1	1.4
GYPSUM	.9	1.7	1.8	.2	2.8	44.8	.6	.1	.2	45.2	.1	1.6
BARITE	1.3	2.7	.2	.0	.4	1.8	2.5	.7	.0	42.6	45.7	2.2
APATITE	.8	.8	1.3	.1	25.6	67.1	.4	.3	.3	1.8	.6	.9
CA AL-P	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
KCL	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
GYPSUM/BARITE	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
GYPSUM/AL-SILIC	29.4	21.3	3.1	.7	3.3	16.5	1.3	.4	2.7	17.7	.7	2.9
SI-RICH	75.2	10.5	2.5	.2	.8	1.6	.4	.3	2.5	3.6	.8	1.6
CA-RICH	3.9	3.3	7.2	.3	3.1	72.0	2.3	.6	.5	4.0	1.1	1.8
CA-SI RICH	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
UNCLASSIFIED	24.0	15.7	14.0	1.3	2.9	14.6	2.5	.6	3.4	16.9	1.2	2.9

APPENDIX D

ENERGY-DISPERSIVE CHEMICAL DATA FOR LA ROBLA I ASH DEPOSITS

Table D-1. Baseline 8/21 Test

Table B-1. Baseline 6/21 Test										
Matrix										
Sample	UF947	UF947	UF948	UF949	UF950	UF951	UF951			
	NE	NE Level	SW	NW	SE Level	NE Level	NE Level			
Location	Level 2	2	Level 1.5	Level 1.5	2	1.5	1.5			
Na	0.19	0.2	0.07	0.11	0.26	0.4	0.09			
Mg	2.49	2.5	1.98	2.41	3.01	2.18	2.22			
Al	14.38	14.11	13.99	12.37	13.7	8.39	8.59			
Si	44.25	44.72	32.85	34.63	53.26	32.99	32.48			
P	1.49	1.28	0.66	0.96	1.95	1.98	1.73			
S	0	0	0.11	0.17	0	0.09	0			
Cl	0	0.21	0.04	0.02	0.19	0	0			
K	8.14	7.99	4.53	6.05	12.36	3.56	2.88			
Ca	12.78	13.11	17.95	22.33	6.62	30.36	29.91			
Ti	0.86	0.88	1.21	1.89	0.23	1.32	0.2			
Cr	0	0.11	0.1	0.54	0	0.03	0.33			
Fe	15.43	14.9	25.98	18.51	6.76	17.76	19.31			
Ba	0	0	0.53	0	1.65	0.95	2.26			
Crystal										
Sample	UF947	UF947	UF948	UF948	UF949	UF949	UF949	UF950	UF951	UF951
	NE	NE Level	SW	SW	NW	NW	NW	SE	NE Level	NE Level
Location	Level 2	2	Level 1.5	Level 1.5	Level 1.5	Level 1.5	Level 1.5	Level 2	1.5	1.5
Na	0.35	0.17	0.09	0.15	0.1	0.07	0.26	0.36	0	0.18
Mg	0.09	0.19	0	0.12	0.26	0.12	1.02	0.25	0.1	0.28
Al	26.45	25.87	26.79	25.96	25.99	25.44	21.04	27.55	25.68	25.99
Si	38.03	38.46	35.71	37.27	36.78	37.1	35.72	38.9	35.49	35.98
P	0.14	0.15	0.12	0	0	0.03	0.25	0.09	0	0.11
S	0.01	0	0.12	0.12	0.1	0	0.06	0	0.06	0
Cl	0	0.07	0.15	0	0	0.03	0	0.06	0.02	0
K	1.2	0.94	0.57	0.71	1.36	0.8	2.08	1.26	0.42	0.46
Ca	28.43	28.2	29.47	29.09	28.89	30.15	26.7	27.77	30.45	29.45
Ti	0.12	0	0	0	0	0.39	0.55	0	0.34	0
Cr	0.04	0.05	0	0.28	0	0	0	0	0	0.24
Fe	4.77	5.52	6.29	6.31	5.56	5.86	12.32	3.04	7.45	6.99
Ba	0.36	0.39	0.7	0	0.96	0	0	0.73	0	0.32

Continued. . .

Table D-1. Baseline 8/21 Test (continued)

Grains										
Sample	UF947	UF947	UF948	UF948	UF949	UF949	UF950	UF950	UF951	UF951
	NE	NE Level	SW	SW	NW	NW	SE Level	SE	NE Level	NE Level
Location	Level 2	2	Level 1.5	Level 1.5	Level 1.5	Level 1.5	2	Level 2	1.5	1.5
Na	0.03	0.1	0.13	0.02	0.34	0.09	0.19	0	0.14	0.18
Mg	0.42	0.47	0.38	0.29	0.65	0.58	1.1	1.38	0.41	1.8
Al	3.51	3.14	3.18	16.39	2.09	1.95	2.65	2.61	1.05	5.21
Si	0.21	2.4	0.25	19.53	0.16	0.14	0.45	0.28	0.02	13.54
P	0.03	0	0.05	0.07	0.04	0	0.04	0.07	0.01	0.28
S	0.04	0	0	0.13	0	0	0	0.01	0.04	0.12
Cl	0.1	0	0.09	0.04	0	0	0	0	0	0.01
K	0.05	0.44	0	0.37	0.07	0.2	0.3	0.23	0.03	0.04
Ca	0.25	0.73	0.38	17.45	0.37	0.51	0.46	0.08	0.02	17.25
Ti	2.59	3.64	3.61	1.52	3.77	3.21	4.67	4.97	2.27	1.22
Cr	0	0.13	0	0.14	0.11	0.43	0	0.21	0	0.15
Fe	92.78	88.95	91.93	43.26	92.39	92.29	90.14	90.17	96.01	60.21
Ba	0	0	0	0.79	0	0.59	0	0	0	0

Table D-2. O₂ Test

Matrix

Sample Location	UF952 NE Level 2	UF952 NE Level 2	UF953 NW Level 1.5	UF953 NW Level 1.5	UF954 NE Level 1.5	UF954 NE Level 1.5	UF954 NE Level 1.5	UF955 SE Level 2	UF955 SE Level 2	UF956 SW Level 1.5	UF956 SW Level 1.5
Na	0.22	0.01	0.19	0.3	0.58	0.22	0.22	0.26	0	0.39	0
Mg	1.75	1.74	2.12	2.46	3.25	2.59	2.59	3.62	3.21	2.72	2.83
Al	14.33	14.25	12.51	12.8	13.18	12.67	12.67	10.74	10.75	10	9.76
Si	38.21	37.25	31.7	32.05	43.7	43.91	43.91	36.29	36.13	37.44	37.32
P	1.04	1.02	0.7	0.8	1.27	1.66	1.66	1.72	1.47	0.8	1.24
S	0	0.16	0	0	0	0.19	0.19	0.13	0	0	0.26
Cl	0.05	0	0	0.22	0	0	0	0	0.28	0.17	0.06
K	6.39	6.31	3.9	4.51	7.38	7.64	7.64	5.1	4.38	4.96	5.87
Ca	14.9	16.67	20.85	20.15	16.32	14.56	14.56	24.33	23.93	22.48	21.76
Ti	1.45	1.33	0.56	0.56	1.75	1.32	1.32	1.79	1.1	0.85	1.21
Cr	0.22	0.03	0	0.21	0.03	0	0	0	0.38	0.11	0
Fe	21.43	20.63	26.23	24.52	12.31	15.23	15.23	16.01	18.16	19.11	19.11
Ba	0	0.6	1.24	1.43	0.22	0	0	0	0.22	0.96	0.59

Crystal

Sample Location	UF952 NE Level 2	UF952 NE Level 2	UF953 NW Level 1.5	UF953 NW Level 1.5	UF954 NE Level 1.5	UF954 NE Level 1.5	UF954 NE Level 1.5	UF955 SE Level 2	UF955 SE Level 2	UF956 SW Level 1.5	UF956 SW Level 1.5
Na	0.19	0.09	0	0.39	0.23	0	0	0	0.06	0.22	0.03
Mg	0	0.12	0.05	0	0.06	0.76	0.76	0.18	3.16	0.76	0.22
Al	25.92	25.98	26.33	25.71	23	24.28	24.28	26.3	27.6	22.89	25.96
Si	37.59	37.21	36.14	35.67	38.39	37.96	37.96	36.65	29.43	36.63	37.37
P	0.16	0.12	0	0	0.29	0	0	0.31	0.28	0.32	0
S	0.02	0.24	0	0.33	0.13	0	0	0.15	0.05	0	0
Cl	0.12	0.04	0	0.14	0	0	0	0	0	0	0
K	1.29	1012	0.72	0.85	1.72	2.04	2.04	0.84	0.25	1.81	0.55
Ca	27.96	28.21	29.69	30.99	28.4	27.39	27.39	29.04	23.4	27.24	29.77
Ti	0.36	0	0	0	0.52	0	0	0.37	0.1	0.85	0
Cr	0.02	0.09	0	0.05	0	0	0	0	0.13	0.07	0.69
Fe	6.36	6.37	7.07	5.87	7.26	7.57	7.57	6.16	15.14	9.22	5.27
Ba	0	0.42	0	0	0	0	0	0	0.39	0	0.15

Continued...

Table D-2. O₂ Test (continued)

Grain										
Sample	UF952	UF952	UF953	UF953	UF954	UF954	UF955	UF955	UF956	UF956
Location	NE Level	NE Level	NW Level	NW Level	NE Level	NE Level	SE Level	SE Level	SW Level	SW Level
	2	2	1.5	1.5	1.5	1.5	2	2	1.5	1.5
Na	0.08	0.26	0	0.05	0.13	0.29	0	0.14	0.15	0
Mg	3.02	2.38	0.36	0.43	0.85	0.63	0.93	0.76	0.29	0.39
Al	5.24	4.76	2.05	2.43	2.34	1.82	5.6	9.52	1.63	1.74
Si	0.16	0.14	0	0.1	0.17	0.57	5.3	12.17	0.15	0.37
P	0.01	0	0	0	0.08	0.1	0	0	0.08	0.15
S	0.05	0	0	0.06	0	0.07	0	0.15	0	0.04
Cl	0.01	0	0	0.2	0.15	0	0.44	0.24	0	0.16
K	0.11	0	0	0.16	0.18	0.23	0.22	0.5	0.03	0.06
Ca	0.01	0.33	0.17	0	0	0.44	3.11	7.99	0.62	0.47
Ti	0.5	0.68	2.67	2.78	3.64	3.22	3.41	1.87	1.41	2.08
Cr	0.2	0	0.04	0.38	0	0	0	0.02	0	0.18
Fe	90.61	91.44	94.71	91.67	91.33	92.63	80.61	64.23	95.63	94.23
Ba	0	0	0	1.73	1.13	0	0.38	2.41	0	0.12

Table D-3. Baseline Test 2

Matrix						
Sample	UF957	UF957	UF958	UF958	UF959	UF959
Location	SE Level 2	SE Level 2	NW Level 2	NW Level 2	SW Level 1.5	SW Level 1.5
Na	0.12	0	0.37	0.06	0.56	0
Mg	3.43	3.15	3.82	3.05	0.27	0.49
Al	5.77	8.27	9.9	10.07	22.63	24.5
Si	32.56	31.33	35.71	36.32	35.58	35.23
P	2.19	1.3	1.54	1.81	0.1	0.02
S	0	0	0.15	0.42	0	0
Cl	0	0.13	0.1	0	0	0.06
K	2.8	2.98	7.15	7.1	1.7	1.99
Ca	30.08	28.32	21.37	23.39	27.9	20.92
Ti	1.22	3.04	0.27	1.04	0.56	0.83
Cr	0	0	0.22	0.27	0.48	0
Fe	20.99	21.48	18.07	15.57	10.21	15.96
Ba	0.85	0	1.33	0.91	0	0
Crystal						
Sample	UF957	UF957	UF958	UF958	UF959	UF959
Location	SE Level 2	SE Level 2	NW Level 2	NW Level 2	SW Level 1.5	SW Level 1.5
Na	0	0.1	0.41	0.07	0	0.26
Mg	0.14	0.24	0	0	2.32	4.66
Al	23.84	24.71	24.09	26.32	12.01	5.84
Si	35.9	37.75	35.49	36.17	20.08	25.98
P	0.34	0.55	0.05	0	0	0.1
S	0	0.32	0	0.14	0	0.11
Cl	0.49	0	0.38	0.2	0.13	0
K	1.37	1.65	1	0.66	0.21	0
Ca	29	27.57	29.49	29.31	29.11	31.21
Ti	0	0.38	0.02	0.07	0.23	0.67
Cr	0	0	0	0	0	0.54
Fe	7.77	6.72	9.07	7.07	35.9	30.64
Ba	1.14	0	0	0	0	0

Table D-3. Baseline Test 2 (continued)

Grains

Sample Location	UF957 SE Level 2	UF957 SE Level 2	UF958 NW Level 2	UF958 NW Level 2	UF959 SW Level 1.5	UF959 SW Level 1.5
Na	0	0.45	0.09	0.48	0.11	0
Mg	0.21	0.78	0.67	0.66	0.17	0
Al	6.7	0.88	2.37	1.73	0.08	0.14
Si	6.96	0.16	0	0.16	97.06	0.11
P	0.21	0.04	0	0	0	0.06
S	0	0.01	0	0.13	0	0
Cl	0.48	0.45	0.02	0.08	0.54	0.03
K	0	0.18	0.2	0.11	0.17	0
Ca	5.35	0.53	0.4	0.65	0.7	0.67
Ti	1.01	2.91	3.31	2.55	0	0.94
Cr	0.81	0.11	0.54	0.54	0.54	0.27
Fe	76.93	93.5	92.41	92.21	0.72	97.67
Ba	1.32	0	0	0.7	0	0.12

Table D-3. Burner Vein Rod Test

Matrix						
Sample	UF960	UF960	UF961	UF961	UF962	UF962
Location	NW Level 2	NW Level 2	SE Level 2	SE Level 2	NW Level 1.5	NW Level 1.5
Na	0	0	0.18	0.29	0.26	0.14
Mg	2.91	2.38	2.93	2.59	2.56	2.8
Al	12.37	12.31	11.07	10.58	11.65	10.33
Si	36.98	36.44	35.11	37.36	30.75	31.65
P	1.29	0.72	1.3	0.93	1.28	1.18
S	0	0	0.05	0	0.08	0.09
Cl	0.04	0	0.03	0.03	0.36	0.32
K	5.8	6.36	6.75	7.26	3.37	4.52
Ca	19.65	17.57	23.03	22.81	23.87	24.87
Ti	0	1.28	1.59	1.58	0.82	1.31
Cr	0.35	0.57	0	0.34	0.1	0
Fe	20.61	22.38	17.37	16.22	22.88	22.78
Ba	0	0	0.57	0	2.03	0

Crystal
Sample

	UF960	UF960	UF961	UF961	UF962	UF962
Location	NW Level 2	NW Level 2	SE Level 2	SE Level 2	NW Level 1.5	NW Level 1.5
Na	0.09	0.21	0.04	0.09	0.44	0.1
Mg	0.05	0.04	0	0.21	1.06	1.02
Al	26.22	25.27	24.62	36.83	23.05	19.48
Si	36.89	37.77	35.26	36.19	34.66	33.77
P	0	0.04	0.18	0	0.44	0.25
S	0	0.03	0.48	0	0	0
Cl	0	0.57	0	0	0.14	0.03
K	0.58	1.24	0.74	0	1.76	3.37
Ca	30.11	28.48	30.18	30.15	27.26	25.72
Ti	0.39	0	0.33	0	0.73	0.37
Cr	0.43	0.19	0	0.28	0	0
Fe	5.2	6.16	8.18	6.25	10.47	13.64
Ba	0.05	0	0	0	0	2.24

Table D-3. Burner Vein Rod Test (continued)

Grains

Sample Location	UF960 NW Level 2	UF960 NW Level 2	UF961 SE Level 2	UF961 SE Level 2	UF962 NW Level 1.5	UF962 NW Level 1.5
Na	0.05	0.29	0.56	0	0.18	0.23
Mg	0.43	0.7	1.48	1.49	0.69	0.88
Al	2.83	2.24	4.7	2.91	2.04	3.4
Si	0.09	0.37	11.84	6.66	0.15	3.42
P	0.03	0	0.2	0.25	0	0
S	0	0	0.38	0.19	0	0.06
Cl	0	0	0	0.25	0	0
K	0.14	0.04	1.89	1.28	0.11	0.41
Ca	0.14	0.07	6.79	3.83	0.68	2.27
Ti	3.31	3.81	3.75	3.1	3.01	2.65
Cr	0.4	0.44	0.36	0.21	0	0.36
Fe	91.53	92.03	68.04	79.56	91.85	85.35
Ba	1.04	0	0	0.27	1.3	0.96

APPENDIX E

OPTICAL PYROMETER MEASUREMENTS

Table E-1. Baseline 8/21 Test

LaRobla									
Level	2	8/21/2002	2	NE	2	NW	2	SW	1.5
Port	SE								SW
Time	11:00			11:08		11:19		11:27	11:36
Flame	orange/yellow		orange/bright yellow	orange/bright yellow	orange/ashes	bright yellow	orange/yellow	flashes	yellow
Deposit	1/2 cm above pt		1/2 cm molten?			1/2 cm left of port		little deposit	1 cm at port
Average Temp. in °C	1205		1357		1213		1253		1531
	1224		1383		1258		1254		1553
	1243		1415		1274		1272		1547
Average	1224		1385		1248		1260		1544
Peak Temp. in °C	1280		1590		1450		1318		1573
	1304		1629		1382		1323		1565
	1325		1589		1472		1324		1552
Average	1303		1603		1435		1322		1563
Sample	yes		yes		yes		NA		yes
			2 samples, 2nd slag running down						
Notes	NA		from top		NA		gas going up!		NA

Continued...

Table E-1. Baseline 8/21 Test (continued)

Level	1.5	1.5	1.5	6	6.5	6.5
Port	NW	SE	NE	NW	NW	SW
Time	11:42	11:51	11:56	12:07	12:12	12:18
Flame	bright yellow	bright yellow	bright yellow pulsing	medium orange	dull orange	dull orange
Deposit	0.5 cm slag side and top	port has slag	<1/2 cm	1-2 cm on inside	1 cm	1 cm
Average Temp in °C	1563	1576	1628	1254	1162	1200
	1539	1579	1570	1248	1155	1213
	1537	1574	1605	1251	1155	1202
Average	1546	1576	1601	1251	1157	1205
Peak Temp. in °C	1576	1579	1655	1251	1179	1218
	1568	1586	1658	1259	1170	1218
	1559	1585	1645	1264	1178	1238
Average	1568	1583	1653	1258	1176	1225
Sample	yes	no	yes	NA	NA	NA
Notes	NA	port blocked 1 cm hole	NA	NA	NA	tubes hard to see

Continued. . .

Table E-1. Baseline 8/21 Test (continued)

Level	6	6.5	6	2	1.5	1.5	2
Port	NE	NE	NW	SW	SW	NW	NE
Time	17:02	17:07	17:13	17:39	17:45	17:50	17:20
Flame	bright orange	dull orange	dull orange	dull orange-bright orange	yellow	yellow/bright yellow	orange bright yellow
Deposit	2 cm?	0.5 cm	1 cm	No	1/2 cm bottom	1-2 cm bottom	pulse
Average Temp. in °C	1239	1163	1178	1220	1522	1533	1328
	1211	1109	1183	1220	1533	1549	1366
	1236	1157	1111	1221	1533	1558	1319
Average	1229	1143	1157	1220	1529	1547	1338
Peak Temp. in °C	1254	1171	1203	1260	1532	1580	1595
	1266	1171	1219	1249	1539	1562	1649
	1258	1155	1218	1242	1557	1546	1636
Average	1259	1166	1213	1250	1543	1563	1627
Sample	NA	NA	NA	No	Yes	Yes	Yes
Notes	NA	NA	NA	NA	NA	NA	temps jumping 1200-1400

Table E-2. O₂ Test

8/22/2002									
Level	2	1.5	1.5	6.5	6	2	2		
Port	SE	SE	NE	NW	NE	SW	NW		
Time	17:26	17:55	18:00	8:46	8:52	9:01	9:06		
Flame	orange yellow streaks	bright orange/yellow	yellow	Orange	Orange	dull orange	dull yellow		
Deposit	slag 1 cm top	1.5-2 cm left of port	1 cm Right	NA	NA	cm	0.5 cm left		
Average Temp. in °C	1208	1396	1549	1164	1206	1047	1252		
	1227	1428	1566	1148	1213	1053	1356		
	1240	1402	1570	1160	1213	1016	1322		
Average	1225	1409	1562	1157	1211	1039	1310		
Peak Temp. in °C	1337	1506	1589	1191	1249	1092	1466		
	1325	1531	1574	1188	1257	1092	1354		
	1298	1532	1590	1191	1234	1075	1480		
Average	1320	1523	1584	1190	1247	1086	1433		
Sample	Yes	Yes	Yes	NA	NA	No	Yes		
Notes	NA	NA	NA	puffing gently	puffing gently	sparkles up	NA		

Continued. . .

Table E-2. O₂ Test (continued)

Level	1.5	1.5	2	2	1.5
Port	SW	NW	SE	NE corner	SE
Time	9:11	9:15	9:20	9:25	9:30
Flame	yellow-flashes of orange	yellow	dull yellow flickering	yellow-bright to dark flickering	yellow
Deposit	little	little	0.3 cm	no deposit	port plugged
Average Temp. in °C	1411	1517	1305	1409	1488
	1415	1497	1272	1432	1502
	1372	1490	1294	1334	1498
Average	1399	1501	1290	1392	1496
Peak Temp. in °C	1453	1594	1335	1448	1496
	1432	1591	1324	1548	1513
	1447	1581	1432	1492	1498
Average	1444	1589	1364	1496	1502
Sample	No	NA	Yes	No	No
Notes	NA	NA	NA	NA	NA

Continued. . .

Table E-2. O₂ Test (continued)

Level	1.5	6.5	6.5	6	2
Port	NE	NW	NE	NE	SW
Time	9:33	13:42	13:47	13:52	14:04
Flame	bright to dull yellow flickering	orange	orange	orange	dull orange, flashes yellow, sparklers
Deposit	No	NA	NA	NA	none
Average Temp in °C	1528	1202	1136	1228	1110
	1529	1195	1141	1229	1111
	1523	1195	1145	1213	1121
Average	1527	1197	1141	1223	1114
Peak Temp. in °C	1592	1218	1163	1251	1100
	1596	1211	1151	1253	1133
	1583	1212	1156	1242	1133
Average sample	1590	1214	1157	1249	1122
	No	NA	NA	NA	No
notes	NA	NA	Moderate puffing	NA	NA

Continued. . .

Table E-2. O₂ Test (continued)

Level	2	1.5	1.5	2	2	1.5
Port	NW	SW	NW	SE	NE	SE
Time	14:09	14:15	14:19	14:26	14:31	14:36
Flame	orange, flashes yellow, sparklers	yellow little bit	yellow drip-hard	dull orange to orange 0.5 cm	flash, yellow to orange sparklers no	yellow plugged
Deposit	0.2 cm					
Average Temp. in °C	1318	1464	1407	1281	1289	1482
	1152	1466	1473	1274	1219	1472
	1311	1438	1438	1268	1257	1487
Average	1260	1456	1439	1274	1255	1480
Peak Temp. in °C	1463	1518	1517	1325	1430	1512
	1380	1478	1536	1354	1380	1525
	1437	1512	1539	1356	1485	1503
Average	1427	1503	1531	1345	1432	1513
sample	Yes	No	Yes	Yes	No	No
Notes	NA	NA	NA	NA	Na	NA

Table E-3. Burner Vein Rod Test

		8/20/2002			
Level	1.5	2	2	2	2
Port	NE	SE	NE	SW	NW
Time	14:39	NA	NA	9:23	9:26
Flame	bright yellow	orange-dull	dull orange flame	orange-dull orange/dark	orange-brightest of 4
Deposit	hard, small amt	NA	no deposit on tubes	pulsing sparklers	large 8cm at left
Average Temp in °C	1508	NA	NA	no new deposit	NA
	1518	NA	NA		NA
	1565	NA	NA		NA
Average	1530	NA	NA		NA
Peak Temp. in °C	1650	NA	NA		NA
	1603	NA	NA		NA
	1569	NA	NA		NA
Average	1607	NA	NA		NA
Sample	No	NA	NA		NA
			port full of black		
Notes	NA	NA	powder	NA	easily removed

Continued. . .

Table E-3. Burner Vein Rod Test (continued)

Level	1.5	1.5	1.5
Port	SW	NW	SE
Time	NA	NA	NA
Flame	orange-yellow sparklers	yellow, orange flickers	yellow steady
Deposit	1/2 blocking port left and right	large deposit below port	1 cm hole, port blocked
Average Temp in °C	NA	NA	NA
	NA	NA	NA
	NA	NA	NA
Average	NA	NA	NA
Peak Temp. in °C	NA	NA	NA
	NA	NA	NA
	NA	NA	NA
Average	NA	NA	NA
Sample	NA	NA	NA
Notes	deposit soft dry to slightly sticky	deposit soft, dry to slightly sticky	molten honey like ash in center hole

Continued. . .

Table E-3. Burner Vein Rod Test (continued)

Level	1.5	2	2
Port	NE	NE	NW
Time	NA	12:39	
Flame	orange flame pulsing darker, flashes yellow	dull orange/dark streaks, few sparklers	dull orange/dark streaks, few sparklers
Deposit	above port	no	small growth size
Average Temp in °C	NA	NA	NA
	NA	NA	NA
	NA	NA	NA
Average	NA	NA	NA
Peak Temp. in °C	NA	NA	NA
	NA	NA	NA
Average	NA	NA	NA
Sample	NA	NA	NA
Notes	dry, shedding	NA	taken

Continued. . .

Table E-3. Burner Vein Rod Test (continued)

Level	2	2	1.5	1.5	1.5	1.5
Port	SW	SE	NE	SE	SW	NW
Time	12:49	12:53	12:57	13:02	13:05	13:08
Flame	dull/bright orange	few sparks flame orange	yellow -orange	bright yellow	bright yellow	orange/yellow pulse
Deposit	none	NA	1 cm	no	1.5 cm left	1 cm left of port
Average Temp in °C	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
Average	NA	NA	NA	NA	NA	NA
Peak Temp. in °C	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
Average	NA	NA	NA	NA	NA	NA
Sample	NA	taken	taken		taken	taken
Notes		NA	shedding dep. Very soft	NA	black, hard	NA

Continued...

Table E-3. Burner Vein Rod Test (continued)

Level	2	2	2	2
Port	SE	NE	SW	NW
Time	15:23	15:32	15:38	15:42
Flame	orange/few sparks, yellow streaks dull orange/orange dull orange/orange flicker dull/bright orange, yellow flashes			
Deposit	1-2 cm	no	NA	1 cm left of tube
Average Temp. in °C	NA	NA	NA	NA
	NA	NA	NA	NA
	NA	NA	NA	NA
Average	1195	NA	1202	1193
Peak Temp. in °C	NA	NA	NA	NA
	NA	NA	NA	NA
	NA	NA	NA	NA
Average	1310	NA	1279	1249
sample	taken	NA	NA	taken
notes	soft	large fluctuations	NA	soft, slightly molten

Continued. . .

Table E-3. Burner Vein Rod Test (continued)

Level	1.5	1.5	1.5	1.5	6.5
Port	SW	NW	NE	SE	NW
Time	15:50	15:58	16:07	16:10	16:22
Flame	bright yellow	yellow flashes, bright orange	yellow flashes	yellow bright flame	dull orange
Deposit	1 cm left of port	2 cm across bottom of port	0.5 cm at top of port	port plugged	1 cm on W side of tube
Average Temp. in °C	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA
Average	1495	1451	1552	1557	1133
Peak Temp. in °C	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA
Average	1533	1473	NA	NA	NA
Sample	taken	taken	taken	NA	NA
Notes	soft	soft, semimolten	NA	NA	no tubes in reach

Continued. . .

Table E-3. Burner Vein Rod Test (continued)

8/21/2002						
Level	6	6.5	6	2	2	2
Port	NW	SW	NW	SE	NE	NW
Time	NA	NA	NA	8:56	NA	9:01
Flame	dull orange	bright orange	NA	NA	NA	NA
	1-2 cm on					
Deposit	tubes	0.5cm	port plugged	port closed over	1 cm	NA
Average Temp. in °C	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
Average	1221	1139	NA	NA	NA	NA
Peak Temp. in °C	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
	NA	NA	NA	NA	NA	NA
Average sample	NA	NA	NA	NA	NA	NA
	out of reach	hard to see, out of reach	NA	molten on inside like HTE not slag	molten, easily removed	NA
notes						

Continued. . .

Table E-3. Burner Vein Rod Test (continued)

Level	2	1.5	1.5	1.5
Port	SW	SW	NW	SE
Time	9:03	9:04	9:07	9:10
Flame	NA	NA	NA	NA
Deposit		1 cm right	port half closed	
Average Temp. in °C	dep. at right	and top	bottom	port plugged molten slag
	NA	NA	NA	NA
	NA	NA	NA	NA
	NA	NA	NA	NA
Average Peak Temp. in °C	NA	NA	NA	NA
	NA	NA	NA	NA
	NA	NA	NA	NA
	NA	NA	NA	NA
Average	NA	NA	NA	NA
Sample	NA	NA	NA	NA
Notes	nothing new	NA	soft, center molten	over center hole, really hard slag

Table E-3. Burner Vein Rod Test

Level	1.5
Port	NE
Time	9:12
Flame	NA
Deposit	0.5 in at left and right
Average Temp. in °C	NA
Average. Peak Temp. in °C	NA
Average	NA
Sample	NA
Notes	NA

APPENDIX D

EVALUATION OF UNBURNED CARBON AND SLAGGING PROBLEMS AT UNION FENOSA LA ROBLA I POWER PLANT: PHASE I RESULTS

**EVALUATION OF UNBURNED CARBON
AND SLAGGING PROBLEMS AT
UNION FENOSA LA ROBLA I POWER PLANT:
PHASE I RESULTS**

Prepared for:

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October 2002

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EXECUTIVE SUMMARY

An evaluation of elevated levels of fly ash carbon loss and furnace slagging at Union Fenosa La Robla Unit 1 was performed by the University of North Dakota Energy and Environmental Research Center (UNDEERC) and the Lehigh University Energy Research Center (LUERC). La Robla Station belongs to the Union Fenosa Generating System and has two units rated at 270 and 350 MW, which traditionally burn domestic low-volatile semi-anthracite coals. The carbon burnout in the fly ash and slagging problems are accentuated by the introduction of foreign coals into the fuel pool. Station personnel indicated that fly ash loss of ignition can easily increase by 10 percent when firing foreign coals. The foreign coals fired at La Robla vary in characteristics, composition and grindability in comparison to the design coal. It is believed that other operational and equipment related factors may also contribute to the problems.

A phased approach was proposed to assist Union Fenosa in reducing the severity of the carbon loss/slagging problem. The objective of Phase I is to identify the root causes of the problem and potential cost-effective measures that could be used to solve or minimize the high carbon loss/slagging situation at La Robla. In the second phase, potential solutions will be implemented with the support of field tests.

The first phase evaluation included a review of fuel analysis, furnace design parameters, combustion system operation and unit operating data, as well as observations, discussion with plant operation personnel, and parametric tests performed during a site visit in August 2002. In addition, slagging and fuel reactivity tests will also be performed in Phase I in combination with analysis of slag deposits collected during the site visit. These results will be summarized in a separate report.

The following conclusions and recommendations are issued:

Conclusions

- ◆ Available fuel data indicate that some coals, particularly the Chinese and Sud African, have lower Hardgrove Indexes and lower volatile content. This may lead to poor combustion and high resulting LOI in the fly ash, via coarser coal grinding size and lower fuel reactivity.
- ◆ Operating data indicate that at baseline operating conditions: (1) excessive plugging exists across both regenerative APH's (approximately 255 mm.c.a. pressure drop); (2) average windbox pressure is approximately 40 mm.c.a. lower than typically recommended; (3) average windbox air temperature is approximately 45°C lower than temperatures used in these boilers; (4) the boiler is set at different tertiary register/secondary register/vent damper/flow straightening rod positions than typically used to promote a more staged combustion; (5) coal pipe average air temperatures are approximately 10°C lower than recommended for anthracite fuels; (6) average furnace exit gas temperatures are approximately 200°C higher than design levels; and (7) ESP gas temperature is approximately 15°C higher than specified by the manufacturer. These observations indicate operating conditions that may result in poor secondary air distribution in the windbox, low secondary air jet velocities, insufficient secondary and primary air preheat, off-design flame patterns, accelerated rates of slagging and deteriorated ESP performance, respectively. All these will result in poor combustion and, consequently, high levels of CO and fly ash LOI, specially, when firing off-design coals. The maintenance status of the firing system and secondary air perforated plates may also contribute to the combustion problem.

- ◆ Parametric test data indicate that baseline fly ash LOI, CO, stack dust loading and NO_x emissions are approximately 6.5 percent, 55 ppmv (w.b. at 3 percent O₂), 180 mg/Nm³ and 2,010 mg/Nm³, respectively. A significant excess O₂ stratification was found from gas sampling at the economizer exit. At baseline conditions, levels of O₂ as low as 0.6 percent were found at the center of the furnace, in accordance from the conclusions reached previously. Operation at economizer excess O₂ levels below 3.3 percent were shown to result in increased levels of CO and, potentially, (if firing off-design fuels) fly ash LOI. The maintenance condition of the plant O₂ indication was found to be biased high, which would also contribute to the combustion problem.
- ◆ The parametric test results suggest that manipulation of boiler and burner system control settings could be used in combination with tighter fuel specifications to mitigate the high fly ash LOI slagging problems. However, a test program aimed at finding settings, which result in reasonable levels of unburnt carbon and furnace slagging should consider the tradeoffs between these problems and unit operational and environmental constraints, as well as unit heat rate.

Recommendations

- ◆ It is recommended that foreign fuel specifications be tightened in terms of volatile content and Hardgrove Index. Preferred values for these characteristics are 11 percent and 75, respectively. An engineered coal blending strategy may be helpful in making use of "bad" coals in combination with coals that are more benign to the ash carbon loss/slagging problems
- ◆ It is recommended that air preheaters, pulverizers and firing system be inspected and maintained as required. Of great importance is fixing the air preheater plugging, burner stuck registers and potentially damaged secondary air perforated plates. It is also recommended that plant windbox

pressure and excess O₂ sensors be inspected and calibrated as needed. Coal pipe fuel and dirty-air measurements, and coal fineness tests should be also performed.

- ◆ Adjustments to boiler and firing system control settings would provide a means to reduce the severity of high LOI when firing off-design fuels and to lower upper furnace temperatures to alleviate slagging. It is recommended that a detailed test program be executed to determine the effectiveness of these alternative settings and evaluate their long term performance. Optimal settings should result in lower fly ash LOI and furnace slagging subject to operational and environmental constraints, such as steam temperature/temperating spray levels, unit heat rate penalties, and NO_x emissions and stack dust loading. Testing should be performed at full load conditions and for the most problematic fuels. A load dropping strategy should also be investigated during these tests to determine the impact of reducing a few MW's from peak firing for slagging and combustion improvements. However, this may not be a viable option for a base-loaded boiler as the units at La Robla. Other techniques to improve other problematic areas should also be tested, for example, daily tertiary air register manipulation to remove excessive ash deposit accumulation around the burner nozzles or on the lower furnace refractory walls and ESP power-off rapping to avoid stack opacity excursions.
- ◆ It is recommended that on-line monitoring instrumentation be installed for furnace exit temperature, fly ash sampling and CO indication. Optical and acoustic pyrometers are commercially available for continuous flue gas temperature measurements. Self-aspirated fly ash samplers (known as CEGRIT's) have been extensively applied in the power industry in the U.S. Various options for extractive and across-the-duct techniques for on-line CO indication are also available. Vendor information is attached to this report.

- ◆ Sootblowing optimization and sootblower system upgrading may be useful to reduce furnace exit gas temperatures and reduce slagging. La Robla Unit 1 does not have wallblowers installed in the lower furnace. It is recommended that a sootblowing optimization study and means to upgrade the sootblowing system (more blowers, more effective media, sonic horns) be investigated. Sonic horns have been used in the U.S. to maintain the air preheaters from reaching plugging conditions, but with mixed results.
- ◆ It is recommended that an analytical study be performed of the air flow in- and out-the-windbox. Windbox modifications such as turning vanes and perforated plates to even out the air flow may provide a design solution to the high LOI and slagging problems.

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INTRODUCTION

A visit was done to La Robla Power Station in August 2002 by the University of North Dakota Energy and Environmental Research Center (UNDEERC) and the Lehigh University Energy Research Center (LUERC) to collect information that would be used to evaluate the problems of elevated levels of fly ash carbon loss and furnace slagging in its boilers. La Robla Station belongs to the Union Fenosa Generating System and has two units rated at 270 and 350 MW, which traditionally burn domestic low-volatile semi-anthracite coals. The carbon burnout in the fly ash and slagging problems are accentuated by the introduction of foreign coals into the fuel pool. Fly ash loss of ignition (LOI) can easily increase by 10 percent when firing foreign coals. The foreign coals fired at La Robla vary in characteristics, composition and grindability in comparison to the design coal. It is believed that other operational and equipment related factors may also contribute to the problems. A phased approach was proposed to assist Union Fenosa in reducing the severity of the carbon loss/slagging problem. The objective of Phase I is to identify the root causes of the problem and potential cost-effective measures that could be used to solve or minimize the high carbon loss/slagging situation at La Robla. In the second phase, potential solutions will be implemented with the support of field tests. These solutions should result in minimal impact on unit heat rate and environmental compliance. The results of this work would be useful for providing guidelines for other stations in the Union Fenosa system which experience similar problems.

This report covers the results of a review performed of fuel analysis provided by La Robla Station, the furnace design parameters, combustion system operation, and unit operating data in relation to the carbon loss and slagging problems, as well as observations made during the site visit, discussions with plant operation personnel, and parametric test results. Recommendations are also provided for means of reducing the severity of the problems. As part of the Phase I work, slagging and fuel reactivity tests were planned. The results of this testing, as well as of samples of slag deposits collected during the site visit are reported under a separate report.

UNIT INFORMATION

La Robla Unit 1 was the boiler targeted for this project. This unit is a Foster Wheeler subcritical, natural circulation reheat type boiler with a 100 percent MCR main steam flow rate of 815 Mkg/hr at 168 kg/cm² and 540.5°C at the superheater outlet. The hot reheater has a design flow of 715 Mkg/hr at 38 kg/cm² and 540.5°C. Superheat and reheat steam temperatures are controlled by a combination of steam attemperation, sootblowing and convective pass flue gas damper manipulation (gases split into two separate front and rear convection surface passes of the heat recovery area, for control of reheat steam temperature by proportioning of gases). La Robla Unit 1 is equipped with four D-9 ball mill pulverizers that supply coal to 24 burners grouped in two rows on the front and rear wall, with 6 burners fed by each mill. Each mill provides coal to each side of the boiler to promote a more even distribution of fuel in the furnace.

The Foster Wheeler arch firing system is shown in Figure 1. An inlet distributor at the end of each coal pipe splits the fuel stream to two parallel cyclone burners. The cyclones enrich the mixture going into each burner nozzle by venting some of the air. An adjustable flow straightening device is included in each burner assembly. The amount of vented air leaving the burner body is controlled by the vented air damper located in the vented air pipe. This damper is typically set near the closed position to prevent excessive amounts of fuel fines from the burner vent pipe from by-passing the combustion zone and resulting in high LOI levels in the fly ash. Decreasing the vent damper opening, also increases the velocity of the air-coal mixture and results in a leaner mixture leaving the burner nozzle. Positioning of the straightening vanes into the fuel nozzle minimizes the swirling action of the fuel leaving the cyclone burner and provides an unidirectional fuel stream. The fully inserted position is preferred for complete carbon burnout. This type of flame pattern allows heating of the fuel, while avoiding ignition in close proximity to the fuel nozzle.

The total amount of air which must be supplied to the burners for initial combustion is distributed into primary air and tertiary air. The primary hot air passes from the primary air fans through a tubular air preheater to the mill system, and carries the pulverized fuel to the burners. Preheated tertiary air enters the burner assembly through individual air ducts and flows parallel to the fuel stream as the coal leaves the burner nozzles. Secondary air fans, followed by steam heated coils and regenerative air preheaters, supply air to the front and rear walls below the elevation of the burner arches. In the Foster Wheeler ball mill combustion system for Anthracite type fuel, the secondary and tertiary air amounts to typically 90 percent of the total air and this value remains relatively constant over the entire operating range. The secondary air enters the furnace at an angle to the flame path. The purpose of this is to provide combustion air along the path of the burning fuel for combustion completion. In the lower furnace, a W-shaped flame pattern typically forms. Typical tertiary/secondary air split is 30/70 percent, respectively; and typical secondary air register setting staging is 10/20/30/40 percent from top to bottom.

Figure 1: Low-Volatile Fuel Foster Wheeler Arch Firing System

Figure 2 shows a schematic diagram of the conceptualized air and fuel flows, and combustion zone in the Foster Wheeler arch-fired boiler design. Secondary air is typically staged along the combustion path, with more secondary air to the bottom of the lower furnace, to minimize the quenching effect and provide a longer fuel burnout path. Foster Wheeler literature specifies that the staged secondary air admission and placement of appropriate refractory at strategic locations are important to provide the flame pattern and temperature field required for proper combustion. High degree of carbon burnout is achieved by a combination of long flame residence in the furnace (both downward and upward) and uniform distribution of fuel and air among the various burners along the furnace cross section.

Figure 2: Conceptualized Combustion Pattern in Arch-Fired Boilers

RESULTS OF SITE VISIT AND INFORMATION REVIEW

This section covers the results of a review performed of fuel analysis provided by La Robla Station, the furnace design parameters, combustion system operation, and unit operating data, as well as observations made during the site visit, discussions with plant operation personnel, and parametric test results.

Information on fuel analysis of the coals currently fired at La Robla was provided by the station. Table 1 compares fuel characteristics which are pertinent to the fly ash carbon loss and slagging problems. The data indicates that the foreign coals are relatively low in moisture and ash, consequently, they have higher heating values. In terms of fuel ignitability, all coals are comparable in volatile and hydrogen levels, two parameters typically used to represent fuel reactivity, except the Chinese coal and to some extent the Sud African coal. Fuels which exhibit higher fuel reactivity will be less prone to have combustion problems.

Table 1
La Robla Fuel Characteristics

Fuel	Hardgrove Index	Volatile (%)	Moisture (%)	Ash (%)	H ₂ (%)	Fe ₂ O ₃ (%)	HV, dry (kcal/kg)	Ash Fusion Temp. (deg. C)
Design	75	11.0	12.0	25.0	3.0	n/a	6,000	1,340
Spain	72	11.3	10.8	22.3	2.5	n/a	6,430	1,370
China	52	7.9	5.6	15.1	2.6	3.04	7,140	1,500
Australia	83	11.9	8.0	14.2	3.6	15.9	7,190	1,470
Russia	n/a	11.6	7.0	18.9	n/a	n/a	6,570	n/a
Sud Africa	56	9.8	8.6	16.1	2.8	5.01	6,940	1,410

There are also differences in terms of ash fusion temperatures and the grindability characteristics of these coals. The foreign coals have relatively higher ash fusion temperatures, a rough indication of a lesser slagging potential, however, the Australian coal has a larger percentage of iron oxide in the fuel ash. Large partially oxidized iron (or pyrite) particles are known to be sticky and to be related to slagging on the upper furnace. The Chinese and Sud African coals have lower Hardgrove Indexes. Lower grindabilities indicate coals which are harder to pulverize. The grindability issue may be more relevant at high mill loadings. La Robla Unit 1 is equipped with ball-mills in view of the low grindability and the high fineness required for anthracite fuels. However, boiler manufacturer information on the effect of grindability and fineness on mill capacity indicates that a decrease in coal Hardgrove Index from 75 to 50 percent, at 75 percent through 200 mesh fineness, can have a detrimental impact on the mill capacity factor of approximately 30 percent or, for a constant mill capacity, a

deterioration in coal fineness from 75 to 60 through 200 mesh. No mill fineness information is available at the moment of writing this report. According to plant personnel, La Robla Unit 1 mill fineness stands at around 80 percent passing the 200 mesh on Spaniard coal. We do not have information on the percentage retained on the 50 mesh screen, which is the standard used to determine good combustion in low-NO_x combustion systems. The impact of the foreign coals on these fineness numbers is unknown.

A boiler inspection and personnel consultation was performed during the site visit by the UNDEERC/LUERC team. Operating data was also gathered and analyzed in relation to current operation and, design information and Foster Wheeler recommendations. The following results were found:

- ◆ Mill operating data at full load baseline conditions indicate coal pipe air temperatures ranging from 84 to 87°C. Baseline or reference conditions are those operating settings as-found the first day of testing and preferentially used by the operators. These temperatures are below the 93 to 99°C range recommended for ball mills and anthracite fuels (for a 14 percent volatile content). Higher air coal temperatures assure stable combustion. Although, all four mills were balanced in terms of their amps, Pulverizer-3 was biased in excess of 10 percent in terms of coal loading. Figure 3 displays the pulverizer/coal pipe arrangement for La Robla 1. Pulverizer-3 supplies coal to burners 1, 3, 5 at the Northeast corner and to burners 19, 21 and 23 close to the center of the furnace. Biasing of pulverizers may be motivated by maintenance conditions of the mills. However, this may result in high-temperature, fuel rich conditions that lead to poor combustion.
- ◆ Temperature data obtained from measurements performed with a portable optical pyrometer indicate flue gas temperatures in the furnace and convective pass higher than design values (see Figure 4). Baseline furnace exit gas temperatures (FEGT) were found to be 200°C higher than the design level.

Figure 3: La Robla Unit 1 Pulverizer/Coal Pipe Arrangement

Figure 4: Measured and Design Flue Gas Temperatures for La Robla Unit 1

Higher flue gas temperatures in the upper furnace and around the screen tubes may result in accelerated rates of slag deposition. It should be mentioned that pyrometer calibration and measurement technique may bias the results obtained from these measurements.

- ◆ A review of boiler operating data for the air and gas circuits, indicates some anomalies that may lead to poor windbox air distribution, secondary air penetration and combustion air mixing. All of these potentially result in high localized levels of CO and fly ash LO in the boiler. Excessive plugging was found on both regenerative air preheaters, APH (pressure drop across APH-1 and 2 of 256 and 258 mm.c.a. -approximately 10 in.w.g.- at baseline conditions, respectively). High levels of APH plugging interfere with the normal operation of the boiler air and gas handling system and affect the uniform supply of air to the windbox. The average baseline windbox pressure is approximately 8.4 mm.c.a. (0.33 in.w.g.). This level is too low compared to the design value (50.8 mm.c.a.). It should be noticed that this indication may be due to malfunctioning instrumentation. Windbox air temperature is also low in comparison to design recommendations (355 vs. 400°C). Insufficient air preheat also results in lower windbox pressure and lower secondary air jet velocities, which are needed to promote good combustion. Burner register adjustments are also less effective under low windbox pressures.
- ◆ A survey of burner tertiary and secondary registers, vent dampers and adjustable flow straightening rod positions indicate that contrary to field recommendations for this type of combustion system, the tertiary air register position is predominantly fully open for all burners, the secondary air registers are open at about 30 percent, with no vertical bias. Vent dampers are between 10 to 15 percent open and the adjustable flow straightening rod is partially inserted. La Robla 1 2001 maintenance records indicate the following register settings are typically used during maintenance overhauls: tertiary air, 100 mm; secondary air, 0/40/110/150 mm (20 mm at the corners), vent dampers, 10 mm. The actual positions, at the present time, as well as

the maintenance conditions of the secondary air perforated plates are unknown. Due to the problems associated with the actual design and arrangement of common plenum windboxes and the poor degree of adjustment achievable from this type of register vanes, high LOI in the fly ash may be an indicator and a culprit of erroneous secondary air damper bias, as well as damaged (eroded or slagged) secondary air perforated plates and, as mentioned before, insufficient air preheat.

- ◆ A comparison between the baseline operating flue gas temperature at the entrance of the electrostatic precipitator (ESP) and its design value indicates that the ESP operates at a higher gas temperature than specified (151 vs. 133°C). Ash resistivity is known to be a strong function of temperature. At a typical value of flue gas SO₃ concentration, an extremely sharp rise in ash resistivity can be experienced with increased temperatures. High resistivity can lead to problems such as reduced collecting field strength in the ESP, progressive degradation of the condition of the collecting plates and back corona, all of which reduce ESP collection efficiency and lead to a high stack opacity situation. It should be mentioned here that another factor that impacts fly ash resistivity is the level of unburned carbon in the fly ash. Results of laboratory tests indicate that as the carbon-in-ash level increases above a certain critical level, the resistivity of the ash drops dramatically. This can lead to rapid charge dissipation and, subsequently, particle re-entrainment and high stack opacity.

Parametric testing was performed to determine the impact of boiler control settings on parameters of interest, for example, NO_x and CO emissions, boiler back-end excess O₂ distribution, steam temperatures, fly ash LOI and slag deposits. Testing was performed at full load conditions, while firing national coal and with the unit off grid regulation. Four tests were performed that include different levels of excess air in the boiler and testing the impact of straightening vanes settings on a selected number of burners. Additional testing of other burner/boiler parameters such as secondary/tertiary register opening was hindered by the maintenance condition of the firing system. All

other parameters (i.e., mills loading and oil support firing) were maintained in automatic, but at a constant loading, as possible during the duration of each particular parametric test.

Test procedures include manual data collection from the control room, flue gas sampling from sample ports at the economizer exit, flue gas temperature measurements from selected inspection ports, collection of fly ash samples from the first row of ESP hoppers, and collection of slag deposits from the waterwalls. Fly ash and slag samples were collected after fresh samples accumulated (in the hoppers and on the waterwall, respectively), after the unit achieved steady conditions for the particular test point. Steadiness of the unit was determined by the steam temperature and O₂ probe time traces. Waterwall and convective pass sootblowing was stopped during these tests to avoid interference in the test results from the effect of sootblowing on the parameters of interest. Daily coal samples were collected from the feeders for future analysis.

The following results were obtained:

- ◆ Data were taken with a portable gas analyzer at the economizer exit plane for excess O₂, CO, NO_x and SO₂. Gas samples were extracted from ports adjacent to the plant O₂ analyzers. Figure 5 shows the results for two excess air levels. Air biasing was achieved by manipulating the FD fans output. The results show a situation of air deficiency at the center of the furnace. This may be a consequence of some of the items discussed before: biased mill, insufficient air preheat, low and maldistributed secondary air in the windbox, wrong burner register and component biases, damaged secondary air perforated plate and instrumentation fault.

Figure 5: La Robla Unit 1 Excess O₂ Stratification at the Economizer Exit

- ◆ Figure 6 shows a comparison between the average value of the readings from the four plant O₂ probes and from the four adjacent ports sampled with the portable gas analyzer. The results indicate the expected trend between the combustion air signal and the resulting average excess O₂ at the back-end for the readings taken by the portable instrument. The plant O₂ probes did not exhibit the correct trend. In addition, the data indicate that the plant analyzers are biased high (as much as 1.2 percent), especially at low air flow rates. This implies that the unit may actually run at very low excess air levels due to false plant O₂ probe indication. At the center of the boiler, levels of O₂ as low as 0.6 percent were registered with the portable analyzer at baseline conditions, while the plant O₂ probe in that location indicated between 1.8 and 2.3 percent. Given that this unit is not provided with on-line CO monitors to infer the status of the combustion process, high fly ash LOI levels may be a consequence of this O₂ probe calibration problem. It should be noticed that these measurements may have been affected by the duct geometry and instrument calibration, however, the concerns they raise are valid.

Figure 6: Comparison Between Plant and Analyzer O₂ Readings at La Robla Unit 1

- ◆ The relation between flue gas CO and excess O₂ measured by the gas analyzer is shown in Figure 7. The graph indicates that CO started to substantially increase after the average O₂ level is lowered below the 3.3 percent mark. After the O₂ plant analyzers are re-calibrated, a similar plot would provide a target level of O₂ for the operators to run at. Lower levels of O₂ (below the “knee-of-the-curve”) will result in increased levels of CO and, probably, fly ash LOI with detriment to unit thermal efficiency. The fly ash unburned carbon results from the samples extracted from the ESP hoppers were not conclusive and are plotted in Figure 7 with respect to the average plant O₂ readings. More testing and a more precise sampling procedure such as isokinetic traverses or CEGRIT samplers may be needed for future tests. However, the results indicate that the baseline LOI level for La Robla Unit 1, while burning national coal, is around 6.5 percent.

Figure 7: La Robla Unit 1 CO and Fly Ash LOI Versus Excess O₂

- ◆ Manipulation of boiler and burner system control settings is proposed as a means to mitigate the increase in CO and fly ash LOI levels when burning off-design coals at La Robla Unit 1. These means include increase in excess air and adjustment of burner register biases. These biases are changes in register position from the as found settings. Given the maintenance condition of the unit and time constraints, a through investigation of these parameters was not possible. However, tests were performed at increased excess O₂ and a test was performed where the straightening vanes rod was fully inserted for selected burners (Burners # 7, 8, 9, 19, 20 and 21). No noticeable effect was detected from the latter test. The effect of increasing the excess air level in the boiler is shown in Figures 8, 9 and 10. Figure 8 shows that modest decreases in flue gas temperature can be produced by operating at higher excess O₂ levels.

Figure 8: La Robla Unit 1 FEGT and ESP Gas Inlet Temperature Versus Excess O₂

Figure 9: La Robla Unit 1 Particulate Emissions and Incremental Heat Rate Versus Excess O₂

Figure 10: La Robla Unit 1 FEGT and ESP Gas Inlet Temperature Versus Excess O₂

- ◆ Operating at increased O₂ levels has the combined benefit of reducing FEGT (and consequently slagging), and reducing fly ash LOI and ESP operating temperature (enhancing ESP performance, even at reduced residence times, see Figure 9). Average baseline stack dust loading was found at 180 mg/Nm³. However, steam temperature and NO_x emissions (see Figure 10) were noticed to increase at increased FD fan flows, as well as stack losses, and consequently net unit heat rate. Although, it was informed that La Robla Unit 1 is not subject to NO_x emission limits, current European Unit Directive limits for solids having less than 10 percent volatile is 1,300 mg/Nm³. Based on our measurements, current La Robla average baseline NO_x emission level is 2,010 mg/Nm³. Figure 9 shows the calculated impact of excess O₂ on unit heat rate. These calculations reflect the relative effect of O₂ on unit heat rate based on its incremental impact on some boiler parameters. Future testing should investigate the overall impact of increased levels of excess O₂ in combination with modified burner and mill biases which reduce LOI with minimal impact on stack opacity, NO_x emissions and unit heat rate.

CONCLUSIONS AND RECOMMENDATIONS

An evaluation of elevated levels of fly ash carbon loss and furnace slagging at Union Fenosa La Robla Unit 1 was performed by the University of North Dakota Energy and Environmental Research Center (UNDEERC) and the Lehigh University Energy Research Center (LUERC). These problems become more acute when La Robla Unit 1 fires off-design foreign coals. The evaluation included a review of fuel analysis, furnace design parameters, combustion system operation and unit operating data, as well as observations, discussion with plant operation personnel, and parametric tests performed during a site visit in August 2002. In addition, slagging and fuel reactivity tests will also be performed in Phase I in combination with analysis of slag deposits collected during the site visit. The latter results will be summarized in a separate report.

Conclusions

- ◆ Available fuel data indicate that some coals, particularly the Chinese and Sud African, have lower Hardgrove Indexes and lower volatile content. This may lead to poor combustion and high resulting LOI in the fly ash, via coarser coal grinding size and lower fuel reactivity.
- ◆ Operating data indicate that at baseline operating conditions: (1) excessive plugging exists across both regenerative APH's (approximately 255 mm.c.a. pressure drop); (2) average windbox pressure is approximately 40 mm.c.a. lower than typically recommended; (3) average windbox air temperature is approximately 45°C lower than temperatures used in these boilers; (4) the boiler is set at different tertiary register/secondary register/vent damper/flow straightening rod positions than typically used to promote a more staged combustion; (5) coal pipe average air temperatures are approximately 10°C lower than recommended for anthracite fuels; (6) average furnace exit gas temperatures are approximately 200°C higher than design levels; and (7) ESP gas temperature is approximately 15°C higher than specified by the manufacturer. These observations indicate operating conditions that may

result in poor secondary air distribution in the windbox, low secondary air jet velocities, insufficient secondary and primary air preheat, off-design flame patterns, accelerated rates of slagging and deteriorated ESP performance, respectively. All these will result in poor combustion and, consequently, high levels of CO and fly ash LOI, specially, when firing off-design coals. The maintenance status of the firing system and secondary air perforated plates may also contribute to the combustion problem.

- ◆ Parametric test data indicate that baseline fly ash LOI, CO, stack dust loading and NO_x emissions are approximately 6.5 percent, 55 ppmv (w.b. at 3 percent O₂), 180 mg/Nm³ and 2,010 mg/Nm³, respectively. A significant excess O₂ stratification was found from gas sampling at the economizer exit. At baseline conditions, levels of O₂ as low as 0.6 percent were found at the center of the furnace, in accordance from the conclusions reached previously. Operation at economizer excess O₂ levels below 3.3 percent were shown to result in increased levels of CO and, potentially, (if firing off-design fuels) fly ash LOI. The maintenance condition of the plant O₂ indication was found to be biased high, which would also contribute to the combustion problem.
- ◆ The parametric test results suggest that manipulation of boiler and burner system control settings could be used in combination with tighter fuel specifications to mitigate the high fly ash LOI slagging problems. However, a test program aimed at finding settings, which result in reasonable levels of unburnt carbon and furnace slagging should consider the tradeoffs between these problems and unit operational and environmental constraints, as well as unit heat rate.

Recommendations

- ◆ It is recommended that foreign fuel specifications be tightened in terms of volatile content and Hardgrove Index. Preferred values for these

characteristics are 11 percent and 75, respectively. An engineered coal blending strategy may be helpful in making use of “bad” coals in combination with coals that are more benign to the ash carbon loss/slugging problems

- ◆ It is recommended that air preheaters, pulverizers and firing system be inspected and maintained as required. Of great importance is fixing the air preheater plugging, burner stuck registers and potentially damaged secondary air perforated plates. It is also recommended that plant windbox pressure and excess O₂ sensors be inspected and calibrated as needed. Coal pipe fuel and dirty-air measurements, and coal fineness tests should be also performed.
- ◆ Adjustments to boiler and firing system control settings would provide a means to reduce the severity of high LOI when firing off-design fuels and to lower upper furnace temperatures to alleviate slugging. It is recommended that a detailed test program be executed to determine the effectiveness of these alternative settings and evaluate their long term performance. Optimal settings should result in lower fly ash LOI and furnace slugging subject to operational and environmental constraints, such as steam temperature/temperating spray levels, unit heat rate penalties, and NO_x emissions and stack dust loading. Testing should be performed at full load conditions and for the most problematic fuels. A load dropping strategy should also be investigated during these tests to determine the impact of reducing a few MW's from peak firing for slugging and combustion improvements. Other techniques to improve other problematic areas should also be tested, for example, daily tertiary air register manipulation to remove excessive ash deposit accumulation around the burner nozzles or on the lower furnace refractory walls and ESP power-off rapping to avoid stack opacity excursions.
- ◆ It is recommended that on-line monitoring instrumentation be installed for furnace exit temperature, fly ash sampling and CO indication. Optical and

acoustic pyrometers are commercially available for continuous flue gas temperature measurements. Self-aspirated fly ash samplers (known as CEGRIT's) have been extensively applied in the power industry in the U.S. Various options for extractive and across-the-duct techniques for on-line CO indication are also available. Vendor information is attached to this report.

- ◆ Sootblowing optimization and sootblower system upgrading may be useful to reduce furnace exit gas temperatures and reduce slagging. La Robla Unit 1 does not have wallblowers installed in the lower furnace. It is recommended that a sootblowing optimization study and means to upgrade the sootblowing system (more blowers, more effective media, sonic horns) be investigated. Sonic horns have been used in the U.S. to maintain the air preheaters from reaching plugging conditions, but with mixed results.
- ◆ It is recommended that an analytical study be performed of the air flow in- and out-the-windbox. Windbox modifications such as turning vanes and perforated plates to even out the air flow may provide a design solution to the high LOI and slagging problems.

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