SUBTASK 3.6 – ADVANCED POWER SYSTEMS ANALYSIS TOOLS

Final Report

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SUBTASK 3.6 – ADVANCED POWER SYSTEMS ANALYSIS TOOLS

EXECUTIVE SUMMARY

The use of Energy & Environmental Research Center (EERC) modeling tools and improved analytical methods has provided key information in optimizing advanced power system design and operating conditions for efficiency, producing minimal air pollutant emissions and utilizing a wide range of fossil fuel properties. This project was divided into four tasks: the demonstration of the ash transformation model, upgrading spreadsheet tools, enhancements to analytical capabilities using the scanning electron microscopy (SEM), and improvements to the slag viscosity model. The ash transformation model, Atran, was used to predict the size and composition of ash particles, which has a major impact on the fate of the combustion system. To optimize Atran key factors such as mineral fragmentation and coalescence, the heterogeneous and homogeneous interaction of the organically associated elements must be considered as they are applied to the operating conditions. The resulting model's ash composition compares favorably to measured results. Enhancements to existing EERC spreadsheet application included upgrading interactive spreadsheets to calculate the thermodynamic properties for fuels, reactants, products, and steam with Newton Raphson algorithms to perform calculations on mass, energy, and elemental balances, isentropic expansion of steam, and gasifier equilibrium conditions. Derivative calculations can be performed to estimate fuel heating values, adiabatic flame temperatures, emission factors, comparative fuel costs, and per-unit carbon taxes from fuel analyses. Using state-of-the-art computer-controlled scanning electron microscopes and associated microanalysis systems, a method to determine viscosity using the incorporation of grey-scale binning acquired by the SEM image was developed. The image analysis capabilities of a backscattered electron image can be subdivided into various grey-scale ranges that can be analyzed separately. Since the grey scale's intensity is dependent on the chemistry of the particle, it is possible to map chemically similar areas which can also be related to the viscosity of that compound at temperature. A second method was also developed to determine the elements associated with the organic matrix of the coals, which is currently determined by chemical fractionation. Mineral compositions and mineral densities can be determined for both included and excluded minerals, as well as the fraction of the ash that will be represented by that mineral on a frame-by-frame basis. The slag viscosity model was improved to provide improved predictions of slag viscosity and temperature of critical viscosity for representative Powder River Basin subbituminous and lignite coals.

SUBTASK 3.6 – ADVANCED POWER SYSTEMS ANALYSIS TOOLS

INTRODUCTION

The Energy & Environmental Research Center (EERC) has conducted numerous projects and programs to develop analytical and modeling tools for characterizing fuels and fuel ash by-products and for predicting fuel quality impact on conventional and advanced power system performance. These tools and analytical methods will provide key information that will aid in optimizing system design and operation conditions for efficiency with minimal air pollutant emissions, while utilizing a wide range of fossil fuel properties. The system will be fuel-flexible, allowing for firing of a single or a combination of fuels consisting of coal, natural gas, petroleum coke, and biomass.

The EERC has developed advanced analytical methods to measure key chemical and physical properties of materials that have an impact on power system performance. The series of analytical tools includes computer-controlled scanning electron microscopy (CCSEM) with particle-by-particle capabilities, chemical fractionation, scanning electron microscopy point count (SEMPC), wavelength-dispersive spectroscopy, trace element analysis, and strength-measuring techniques. Modeling tools have also been developed for predicting the formation of ash, deposition on refractory and heat-transfer surfaces, slag flow behavior, and plugging of hot-gas filters. The properties of slags are of importance in the performance of conventional and advanced power systems, with the temperature dependence of slag viscosity affecting slag flow and ash removability and producing undesirable deposition and corrosion issues. An improved method of predicting viscosity and the temperature of critical viscosity is needed to adequately predict basic ash behavior, which is crucial in developing more sophisticated boiler performance models.

PROJECT GOALS AND OBJECTIVES

The goal of this project was to utilize EERC modeling tools and analytical methods to provide key information to aid in optimizing advanced power system design and operation conditions for efficiency, with minimal air pollutant emissions, while utilizing a wide range of fossil fuel properties. The specific tasks included:

- Demonstrate the utility of existing models at the EERC.
- Make improvements to models that have shortcomings that can be corrected efficiently, including prediction of slag viscosity.
- Enhance the application of existing spreadsheet programs developed at the EERC by generating user-friendly revisions and documentation that allow them to be used more conveniently by researchers both at the EERC and outside the center.
- Enhance analytical capabilities to determine the inorganic components in fuels.

STATEMENT OF WORK FOR ACTIVITY 1 – MODEL DEMONSTRATIONS

Activity 1 – Goals and Objectives

The primary models, including FACTTM (commercially available) as well as ATRAN, TraceTran, and Fuel Quality Advisor (developed by the EERC), and viscosity models were compared to actual experimental results from bench-, pilot-, and demonstration-scale advanced power systems in order to investigate any inconsistencies. This was conducted for both gasification and combustion systems. The EERC has significant data available on the performance of a high-temperature advanced furnace system for a wide range of coal types and the transport reactor development unit (TRDU) for a range of fuels. In addition, operating condition information on the fate of major, minor, and trace elements in the system was analyzed.

Activity 1 – Methods

The Ash Transformation module is an integral part of ATRAN, TraceTran, and Fuel Quality Advisor. The module predicts the particle-size distribution along with the major and minor elements. TraceTran is specialized to predict the trace elements in addition to the major and minor elements for a gasification system.

The source code to the Ash transformation code consist of 23 C++ files (.CPP) and 24 header files (.H) which are listed in Table 1. The CPP files contain the algorithms and actual code, while the header files contain definitions of the format and content of functions, constants, and variables used in the respective CPP files.

The standard analyses methods stop the automatic analyses either when 1200 particles have been analyzed (#) or when 100 frames (F#) have been analyzed (each area the SEM can scan without having to move the sample) at each magnification.

This means that the maximum particles entering the program would be data on 3600 particles. However, at the lower magnification analyses, the limit of 100 frames is typically reached before 1200 particles have been found in these size ranges.

The ash transformation algorithm flow diagram is illustrated in Figure 1. The entrained ash PSCD (particle size and composition distribution) is predicted from the distribution of the inorganics in the coal using advanced coal characterization techniques. CCSEM (1), x-ray fluorescence (XRF), and ultimate analysis are used to characterize the major elements in the coal. The CCSEM analysis is also combined with a locked/liberated particle analysis (to determine if the individual mineral grains are located within a coal matrix or are free mineral grains) and ZAF data reduction of the compositions (2, 3). The ZAF data reduction produces compositions free of the effects of atomic number (Z), x-ray absorption (A), and XRF (F). A mass balance is compiled on the coal by comparing the CCSEM and XRF data. The resultant balance provides the compositions of the minerals with their associations to the coal, organically associated constituents, and submicron particles. The trace element concentrations (arsenic, cadmium, chromium, lead, mercury, nickel, and selenium) are determined using variations of atomic adsorption (AA) and inductively coupled argon

TABLE 1

Source Code Files to the Ash Transformation Code Program

CPP Files		Header Files	
ATRAN.CPP	Windows interface to the program Inputs and starts the program	ATRAN.H	Defines max. particles in system, organic-bound Si and % of vaporized elements in size bin <1
ATRAN1.CPP	Data input, data formation, sulfur removal, and fragmentation	ATRAN1.H	Defines ATRAN1
ATRAN2.CPP	Coalescence of included particles	ATRAN2.H	Defines ATRAN2
ATRAN3.CPP	Liberation	ATRAN3.H	Defines ATRAN3
ATRAN4.CPP	Data manipulation of ash, sorts minerals according to size and type of mineral	ATRAN4.H	Defines ATRAN4
ATRAN5.CPP	Mass balances (normalizes and compares data from CCSEM and XRF analyses)	ATRAN5.H	Defines ATRAN5
ATRAN6.CPP	Condensation reactions	ATRAN6.H	Defines ATRAN6
ATRAN7.CPP	Final output of data	ATRAN7.H	Defines ATRAN7
		FORMATS.H	Contains the format for the input and output files to ATRAN
STORAGE.CPP	Handles memory management	STORAGE.H	Defines STORAGE
SPHERES.CPP	V, A, and cross A of spheres	SPHERES.H	Defines SPHERES
GETTYPE.CPP	Returns fragmenting minerals to ATRAN 2	GETTYPE.H	Defines GETTYPE
GETSIZE.CPP	Sort particles into size bins	GETSIZE.H	Defines GETSIZE
GETPHASE.CPP	Writes mineral number for each particle	GETPHASE.H	Defines GETPHASE
FILEIO.CPP	Handles and stores input and output arrays for the seven ATRAN files	FILEIO.H	Defines FILEIO
CONVMAG.CPP	Converts three Mag files into two	CONVMAG.HPP	Defines CONVMAG
COMPOUND.CPP	Mineral classification of CCSEM data from each particle	COMPOUND.H	Defines COMPOUND
COMMON.CPP	Common constants and error messages	COMMON.H	Defines COMMON

Continued . . .

TABLE 1 (continued)

CPP Files		Header Files	
ELEMENTS.CPP	Normalizing routine for the element input	ELEMENTS.H	Defines ELEMENTS
TRACE.CPP	Tracks the trace elements through the ash transformation, lookup tables for four coals, six conditions (C/O, steam), 27 temperatures (1500°–200°C) and six pressures (1–26)	TRACE.H	Defines TRACE
COMATRAN.CPP	Mineral classification of CCSEM data from each particle	COMATRAN.H	Defines COMTRAN
RANDOM.CPP	Random number generator	RANDOM.H	Defines RANDOM

plasma spectroscopy (ICAP). The AA and ICAP techniques are two of the most sensitive techniques for determining trace element concentrations. Each of these techniques has multiple variations that can be used to improve the detection limits for some of the elements.

The minerals are divided into two data sets: those locked within a coal particle and those liberated from the coal matrix. The locked minerals are coalesced, on a frequency basis, in a random fashion with other mineral and submicron particles as well as those organically associated constituents that are expected to condense during the combustion of a coal particle. The coalescence produces intermediate, locked fly ash particles. The liberated minerals do not undergo a coalescence step. Both the intermediate locked particles and liberated minerals are then reacted with those constituents which stay in the vapor phase during the early stages of combustion. During the coalescence and vapor-nucleation steps, the formation of submicron fly ash is predicted. After these steps are completed, three different data sets are formed: locked fly ash, liberated fly ash, and submicron fly ash particles. The three data sets are characterized and combined on a mass basis, giving a distribution of the ash composition as a function of size.

The ash transformation model predicts the vapor content and the PSCD for the ash within a combustion system. The entrained ash PSCD is predicted from the distribution of the inorganics in the coal.

Input File Format for Ash Transformation Model

Input to the ash transformation code consists of coal analysis results determined by CCSEM (1) and standard American Society for Testing and Materials (ASTM) proximate, ultimate, and coal ash chemical analysis methods (Table 2). The CCSEM method provides quantitative information on the distribution of various elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Fe, and Ba) among the mineral constituents of coal, whereas ASTM methods provide information on the bulk chemical composition and combustion characteristics of coal. The combination of these analysis data provide a more comprehensive basis for predicting the combustion performance characteristics of a pulverized coal.

Figure 1. Flow diagram of the Ash Transformation code.

TABLE 2

Ash Transformation Coal and Trace Element Analysis Input Parameters

Method	Parameter(s)	Unit(s)	File Extensions
CCSEM	Elemental mineral compositions	wt%, mineral basis	.ccs
Proximate	Moisture, volatile matter, fixed C, and ash	wt%, as-received	.ult
Ultimate	H, total C, N, S, O, and ash	wt%, as-received	.ult
Coal Chemical Composition	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂ , P ₂ O ₅ , CaO, MgO, Na ₂ O, and K ₂ O	wt%, ash basis	.xrf
Trace Element Bulk	As, Cd, Cr, Pb, Ni, Se, Hg	ppm	.tec
Trace Element Distribution	Trace element distribution among the CCSEM elemental mineral compositions	ppm	.ted

CCSEM Mineral Analysis Results

The CCSEM mineral analysis section consists of either two or three different magnification files. The highest magnification is 800× and is only present with a three-file analysis. The 250× magnification file is either the three-file analysis medium-magnification file or the two-file analysis high-magnification file. The lowest magnification is the 50× file. Each file has 25 columns of data for each mineral particle analysis and a varying number of rows. Each row indicates one mineral particle in the coal matrix. The columns have the following definitions: particle number, chemical type, x-ray count, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ba, Ti, x-coordinate, y-coordinate, average diameter, maximum diameter, minimum diameter, area, perimeter, shape factor, frame number, and excluded/included. The format is as shown in Figure 2.

#	T	Cts	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Ba	Ti	X	Y	Dia	Max	Min	Ar	Pe	Sh	F#	L/L

Explanations: # – particle number, T – Type, Cts – x-ray counts, X – x coordinate, Y – y coordinate, Dia – average diameter, Max – maximum diameter, Min – minimum diameter, Ar – area, Pe – perimeter, Sh – shape factor, F# – Frame number, L/L – locked or liberated particle

Figure 2. Layout of the files from CCSEM analysis.

Ash Coal Chemical Analysis

The chemical composition of coal ash (in wt%) on a sulfur-free basis is also tabulated in a single column, as indicated below, in the following order: SiO₂, Al₂O₃, Fe₂O₃, TiO₂, P₂O₅, CaO, MgO, Na₂O, and K₂O.

Trace Element Bulk Analysis

The trace element bulk composition is in ppm and is also tabulated in a single column in the following order: As, Cd, Cr, Pb, Ni, Se, Hg, and Cl (the chlorine is used in determining thermochemical information; mercury is reported in ng/g).

Coal Proximate and Ultimate Analysis Results

The standard ASTM proximate and ultimate analysis results are reported on an as-received basis in a single column, as indicated in the sample below, in the following order: hydrogen, carbon, nitrogen, sulfur, oxygen, and ash.

Trace Element Distribution Analysis

A file will have nine columns and 33 rows. The rows coincide with the 33 mineral/chemical and mineral association categories classified by the CCSEM analysis. The 33 classifications in order are quartz, iron oxide, periclase, rutile, alumina, calcite, dolomite, ankerite, kaolinite, montmorillonite, potassium aluminosilicate, iron aluminosilicate, calcium aluminosilicate, sodium aluminosilicate, aluminosilicate, mixed silicate, iron silicate, calcium silicate, calcium aluminate, pyrite, pyrrhotite, oxidized pyrrhotite, gypsum, barite, apatite, CaBAIBP, KCl, gypsum/barite, gypsum/aluminosilicate, Si-rich, Ca-rich, CaBSi-rich, and unclassified compositions. The first column indicates the CCSEM classification, the second column is the weight percent of that classification present and columns three through nine are the ppm, on a mineral basis, of the trace elements (As, Cd, Cr, Pb, Ni, Se, and Hg).

Output File Format for Ash Transformation Model

The Major Element Output File contains a table with 33 different ash classifications and six particle sizes. Each ash particle is classified using its chemical composition and particle size. The ash composition classification is done using a best-fit algorithm into one of the following 33 ash compositions: quartz, iron oxide, periclase, rutile, alumina, calcium oxide, derived periclase, calcium–magnesium–iron oxide, dehydrated kaolinite, dehydrated montmorillonite, dehydrated potassium aluminosilicate, iron aluminosilicate, calcium aluminosilicate, sodium aluminosilicate, aluminosilicate, mixed aluminosilicates, iron silicate, calcium silicate, calcium aluminate, iron sulfate, pyrrhotite, oxidized pyrrhotite, gypsum, barium oxide, apatite, Ca–Al–P, KCl, gypsum/barite, gypsum aluminosilicate, Si-rich, Ca-rich, Ca–Si-rich, and unclassified. The classifications were originally developed for coal. The classifications are modified to indicate the changes in the minerals that occur after combustion. This does lead to some repetition in the names, as seen in dolomite changing to derived periclase. The value in the table, as seen in Appendix A, indicates the percentage of ash, on mineral basis, that is in each chemical classification and size bin. In the last column on the right-hand side are the total amounts in each classification. The totals are also totaled at the bottom of the table for each size bin. The amount of total mineral matter is seen at the bottom right-hand corner of the table. The remaining amount is the submicron portion of the ash. The composition of the submicron ash or nucleated ash is given after the entrained ash table. The table in Appendix A also contains the bulk composition of all of the ash in the combustion system. Below these values in the Appendix A table is the breakdown of the bulk composition into

eight different size and type bulk compositions. The eight different bulk compositions are the <1.0- μm ash, 1.0–3.0- μm ash, 3.0–10.0- μm ash, 10.0–30.0- μm ash, 30.0–50.0- μm ash, >50.0- μm ash, entrained ash distribution after size segregation, and the bulk composition of the entrained ash. The entrained ash, less than 10 μm , is the ash that actually goes through the convective pass.

The Trace Element Output File contains three tables, as shown in Appendix B. The first table shows the distribution of the trace elements in ppm by size range in six different size ranges. The last column represents the ash distribution in the convective pass after segregation. The vapor amounts are not included in this table because the vapor elements are assumed to have a negligible mass compared to all of the ash in the system.

The second table shows the distribution of the trace elements by ppm in the seven different size and bulk compositions. The first row is the ppm of trace elements still in vapor phase at the area of interest that the user indicated. The next seven rows are the <1.0- μm ash, 1.0–3.0- μm ash, 3.0–10.0- μm ash, 10.0–30.0- μm ash, 30.0–50.0- μm ash, >50.0- μm ash, and the bulk composition of the trace elements.

The third table indicates the distribution of the trace elements, ppm on a total ash basis, among the 33 CCSEM ash classifications. This table does not include vapor species or ash that is submicron/nucleated. The trace elements associated with the submicron ash are shown in the last two rows.

Experimental values for North Rochelle major and minor elements were compared to values obtained through the Ash Transformation code to note any correlations between actual data and computer-generated data. A similar comparison for the trace elements found in Illinois No. 6 was investigated to note any similarities.

Activity 1 – Results

The trace element ash transformation model (TraceTran) program predicts the vapor content and PSCD of the ash within an entrained gasification system. The model is based on theory and a combination of laboratory- and pilot-scale test data. This program does not contain the various components of operation in a gasifier, such as particulate control, slag partitioning, recycle streams, and multiple heat exchangers. This program accounts for the initial reaction zone and a single heat exchanger and assumes that all of the ash passes through the entire system.

The entrained PSCD is predicted from the distribution of the inorganics in the coal using advanced coal characterization techniques. CCSEM (1), XRF, and ultimate analysis are used to characterize the major elements in the coal. The CCSEM analysis is also combined with a locked/liberated particle analysis (to determine if the individual mineral grains are located within a coal matrix or are free mineral grains) and ZAF data reduction of the compositions (2, 3). A mass balance is compiled on the coal by comparing the CCSEM and XRF data. The resultant balance provides the compositions of the minerals with their associations to the coal, organically associated constituents, and submicron particles. The trace element concentrations (arsenic, cadmium, chromium, lead, mercury, nickel, and selenium) are determined using variations of AA and ICAP),

two of the most sensitive techniques for determining trace element concentrations. Each of these techniques has multiple variations that can be used to improve the detection limits for some of the elements. The minerals are divided into two data sets: those locked within a coal particle and those liberated from the coal matrix. The locked minerals are coalesced, on a frequency basis, in a random fashion with other mineral and submicron particles as well as those organically associated constituents that are expected to condense during the combustion of a coal particle. The coalescence produces intermediate, locked fly ash particles. The liberated minerals do not undergo a coalescence step. Both the intermediate locked particles and liberated minerals are then reacted with those constituents that stay in the vapor phase during the early stages of combustion. During the coalescence and vapor-nucleation steps, the formation of submicron fly ash is predicted. After these steps are completed, three different data sets are formed: locked fly ash, liberated fly ash, and submicron fly ash particles. The three data sets are characterized and combined on a mass basis, giving a distribution of the ash composition as a function of size.

Figures 3 and 4 show the results of testing TraceTran on Illinois No. 6 coal. The first figure contains the PSD predicted by TraceTran and the measured PSD. The “Fuel” category shows how particles are associated in the raw coal. TraceTran did an excellent job of predicting the correct PSD. The second figure has the predicted and measured trace element distribution for the same coal. TraceTran predictions are fair for all trace elements except Pb, Se, and Hg. This is likely a result of the thermal chemical equilibrium tables stored in the code. Additional predictions were done with a Powder River Basin (PRB) coal examining the major/minor element compositions. The results are shown in Appendix C.

Figure 3. PSD in Illinois No. 6 coal.

Figure 4. Distribution of trace elements in particles less than 10 µm.

STATEMENT OF WORK FOR ACTIVITY 2 – INTERACTIVE SPREADSHEET MODEL

Activity 2 – Goals and Objectives

The objective of this task was to enhance the application of existing spreadsheet programs developed at the EERC by generating user-friendly revisions and documentation that allow them to be used more conveniently. The programs contain many useful calculations pertaining to mass balances, heat balances, and overall boiler performance. Programs are also available for gasification and fluidized-bed technologies. Some spreadsheets also model demonstration units at the EERC. The spreadsheets have been combined with reactor residence time distribution calculations to interpret test results from the TRDU. The goal is to validate the calculations and make the programs user-friendly so they appeal to EERC researchers and clients alike.

Activity 2 – Methods and Results

The enhanced interactive spreadsheets integrate correlations of thermodynamic properties for fuels, reactants, products, and steam with Newton Raphson algorithms to perform calculations on mass, energy, and elemental balances; isentropic expansion of steam; and gasifier equilibrium conditions. Derivative calculations can be performed to estimated fuel heating values, adiabatic flame temperatures, emission factors, comparative fuel costs, and per unit carbon taxes from fuel analyses. Example outputs from one of the programs are found in Figures 5 and 6. Most of the spreadsheets require several inputs describing coal chemistry. The outputs below were generated from an ultimate analysis and by specifying a few boiler parameters. Figure 5 contains an example

STEAM CONDITIONS		EFFICIENCIES		
Temp., °F	P, psi	Boiler	Turbine	System
221 °F stack temperature and 50 °F cooling water				
1000	3500	94.64%	49.59%	45.54%
1076	4130	94.64%	50.31%	46.19%
1202	5000	94.64%	52.33%	48.05%

Figure 5. Example of a supercritical steam calculation.

of a supercritical steam calculation. Figure 6 is an example of a material balance. The programs may also have applications in predicting biomass performance.

One of the spreadsheets calculates combustion stoichiometry, moisture- and ash-free heating values, heat and material balances, and adiabatic flame temperatures on the basis of fuel analysis. It also offers comparisons of the cost of power generation for different fuel types, based on the cost of the fuel and characteristic fuel efficiency. The figures show examples of output for each part of the spreadsheet. Figure 7 shows an example of the adiabatic flame temperatures for several fuels at two levels of excess air, as well as calculated heating values and products of combustion. Heat and material balances may also be calculated with this spreadsheet. Macros can be used to adjust flows to satisfy mole balances for H, C, O, S, N, and the overall mass balance; another macro can be used to adjust a specific flow, stream temperature, or heat loss (as a percentage of coal LHV) to satisfy the overall energy balance. Figure 8 is an example of the relative costs of burning several different fuels and includes a calculation for the impact of an energy tax on each fuel.

A considerable effort was made in the improvement of enthalpies used in thermodynamic calculations for several of the programs. Heat capacities were obtained from JANAF tables for the range of temperatures needed in the applications (4–7). A regression analysis was completed to determine a new enthalpy temperature relationship. The new relationships allow more accurate calculations over a broader temperature range than the previous programs. Figure 9 is the format used for the regression analysis of enthalpy data where T K is the temperature in Kelvin and the other variables are simply regression coefficients or constants.

The components used in this analysis as well as the useful temperature ranges and sources are listed below in Table 3. Most of the components are straightforward; however, the elements most commonly found in coal were much harder to evaluate. A brief explanation of the derivation of the enthalpies for sulfur, nitrogen, hydrogen, and oxygen in coal follows.

The enthalpy of organic sulfur is approximated by the enthalpy of sulfur in diphenylsulfide. The percentage of total sulfur occurring as pyrite is treated as a variable in “A,” with the values of “%FeS₂” being either assigned or, in the absence of an assigned value, computed as $0.2 + (9 \times S)$ (e.g., at 5% total sulfur, 65% of the sulfur would be allocated to pyrite and the remainder to organic sulfur). Sulfur as sulfate is neglected. The enthalpy of coal nitrogen is based on N in pyridine.

STREAM NO:	1	2	3	4	5	6	6	PRODUCT GAS	
	INPUT	INPUT	INPUT	INPUT	OUTPUT	OUTPUT	-1	STREAM 6	
STREAM	COAL	STOICH AIR	EXCESS AIR	LIMESTONE	ASH	PER DATA	ADJUSTED	WET GAS	DRY GAS
PARAMETERS	TEMP/ MASS, F,C,lb	TEMP/ MASS, F,C,lb	TEMP/ MASS, F,C,lb	TEMP/ MASS, F,C,lb	TEMP/ MASS, F,C,lb	TEMP/ MASS, F,C,lb	TEMP/ MASS, F,C,lb	ANALYSIS	ANALYSIS
-	-----	-----	-----	-----	-----	-----	-----	-----	-----
TEMP, F	70	650	650	70	3318		3318		
TEMP, C									
H2OG							1.085	13.6%	
H2OL	0.6438						0.000		
N2G	+N	6.90573	1.65737				8.574	69.2%	80.2%
NCOAL							0.000		
O2G	+O	2.09794	0.504				0.504	3.6%	4.1%
H2G							0.000	0.0%	0.0%
C/TAR, SPECIFY H/C					0		0.000		
SULFUR	+S						0.000		
PYRITE							0.000		
S2G							0.000	0.0%	0.0%
COG							0.000	0.0%	0.0%
CO2G							2.622	13.5%	15.6%
SO2G							0.022	0.1%	0.1%
NOG							0.002	0.0%	0.0%
NO2G							0.0%	0.0%	0.0%
CH4G	+C+H						0.0%	0.0%	0.0%
C3H8	+C+H						0.0%	0.0%	0.0%
H2SG							0.0%	0.0%	0.0%
NH3G							0.0%	0.0%	0.0%
COSG							0.0%	0.0%	0.0%
FE2O3									
CaO									
CaCO3				0	0				
CaMg(CO3)2									
CaCl2(s)									
CaCl2(l)									
Ca(OH)2									
CaS									
CaSO4					0.0000		0		
CaSO3									
MAFCOAL	1								
ASH	0.1096				0.0684			100.0%	100.0%
AVERAGE STREAM MW									
-	-	-	-	-	-	-	-	-	-
ENTHALPY BALANCE, Btu	-5218	2441	586	0	-35		2227	(0)	0
HEAT LOSS IN COAL ASH					0.298%			HEAT	NET
NET HEAT LOSS DUE TO ADDITION OF SO2 SORBENT					0.00%			TRANSFER	
-	-	-	-	-	-	-	-	-	-
MATERIAL BALANCE								%ERROR	
#MOLES H	0.12053	0.00000	0.00000	0.00000	-0.00000		-0.12053	-0.00%	#MOLES H
#MOLES C	0.05958	0.00000	0.00000	0.00000	-0.00000		-0.05958	-0.00%	#MOLES C
#MOLES O	0.04908	0.13112	0.03147	0.00000	-0.00000		-0.21167	0.00%	#MOLES O
#MOLES S	0.00034	0.00000	0.00000	0.00000	-0.00000		-0.00034	-0.00%	#MOLES S
#MOLES N	0.00086	0.49327	0.11838	0.00000	-0.00000		-0.61251	-0.00%	#MOLES N
MASS, #	1.75334	9.00368	2.16088	0.00000	-0.06838		-12.80833	-0.32%	MASS, #
-	-	-	-	-	-	-	-	-	-

Figure 6. Example of material balance calculation.

	Natural Gas 96v% CH ₄	Propane, Liquid	Oil	Pennsylvania Bituminous	Kentucky Bituminous	Illinois Bituminous
Calculated adiabatic flame temperature at as-received moisture and ash with air at specified conditions.						
Air Temp., °F	650	650	650	650	650	650
Fuel Temp., °F	70	70	70	70	70	70
AF Burnout	100%	100%	100%	100%	100%	100%
Excess Air 1	0%	0%	0%	0%	0%	0%
Flame Temp., °F	4031	4201	4429	4395	4395	4387
Flame Temp., °C	2222	2316	2443	2424	2424	2419
Excess Air 1	20%	20%	20%	20%	24%	24%
Flame Temp., °F	3485	3597	3740	3861	3782	3764
Flame Temp., °C	1918	1981	2060	2127	2083	2073

Figure 7. Adiabatic flame temperature calculation.

Both oxygen and hydrogen are problematic, since the different forms that may occur affect enthalpy quite differently. Oxygen is considered to be present in four functional forms: 1) hydroxyl form as represented by phenol, 2) ether form as represented by diphenylketone, 3) carbonyl form as in acetophenone, and 4) carboxyl form as in benzoic acid. The first three forms are assumed to remain in a fixed proportion of 2:1:1, while the amount of carboxyl is treated as a function of total oxygen content. The percentage of the oxygen occurring in the carboxyl form is assumed to have a value equal to $1.5 \times O$, so that fuels with very little oxygen contain a negligible amount of carboxyl, and low-rank coals with total oxygen contents of about 20% would be assumed to have 30% of that oxygen occurring as carboxyl, which is reasonable.

For hydrogen, the enthalpy is estimated as a single value for all ranks of coal, even though low-rank coals are generally thought to contain small clusters of aromatic rings and shorter aliphatic chains. Different values of atomic enthalpy for hydrogen are available for hydrogen on a benzene ring and on aliphatics of different chain lengths. The difference is quite important because H-benzene has a positive enthalpy and the H-aliphatic values are all negative. The value for the enthalpy of atomic hydrogen used in “A” is -1700 Btu/lb mole, which is based on 25.7% of the hydrogen being on aromatic rings and the remainder on aliphatic chains of four to ten carbons (an average for C4, C6 and C10 was used). The ~25% aromaticity of hydrogen agrees with values presented by Van Krevelen (8), but no source could be found for an average aliphatic chain length. Attempts were made to improve the correlation by making hydrogen aromaticity a function of coal carbon and oxygen contents, increasing from 20% aromatic at 70% C and 20% O to 30% aromatic at 85% C and 5% O, but this attempted correlation actually increased the spread in the heating values calculated from coal enthalpy, and the approach was abandoned.

The eleven spreadsheet applications have been updated and evaluated; future work on the spreadsheet applications will continue, focusing on creating a comprehensive user’s guide.

		Natural Gas 96% CH4	Propane, Liquid	Oil	Pennsylvania Bituminous	Kentucky Bituminous	Illinois Bituminous
Price Related Factors							
Unit For Pricing for Oil & Propane		mscf	U.S. gal.	bbl	short ton	short ton	short ton
API Gravity				30			
Specific Gravity			0.508	0.88			
LB/BBL or gallon			4.235	306.98			
MILLION Btu/BBL or Btu/gallon			91307	6.06			
\$ PER MM BTU/\$ PER BBL or \$/gal			\$10.9521	\$0.1651			
For Gas							
SCF 60 F/LB		22.98					
Btu/SCF 60 F		1006					
\$ PER MM BTU/\$ PER MSCF		\$1.0056					
For Coal or Other Solid Fuel							
\$ PER MM BTU/\$ PER TON					\$0.0389	\$0.0357	\$0.0406
# C/UNIT (bbl, mscf, gal,ton)		31.48	3.47	257.87	1432.94	1559.41	1308.86
Fuel Cost Factors							
Estimated fuel cost at source, \$/unit		\$3.00	\$0.40	\$35.00	\$33.28	\$24.20	\$30.41
Energy cost, \$/MM Btu HHV		\$3.02	\$4.38	\$5.78	\$1.30	\$0.86	\$1.23
Characteristic generating efficiency, %HHV		50.0%	50.0%	32.8%	33.4%	33.5%	33.2%
Characteristic generating efficiency, %LHV		55.0%	55.0%	34.8%	34.6%	34.7%	34.5%
Lb fuel per MW hr at characteristic HHV efficiency		295.49	316.70	527.96	797.03	728.79	834.30
Fuel cost at characteristic HHV efficiency, \$/MW hr		\$20.60	\$29.91	\$60.19	\$13.26	\$8.75	\$12.69
Maintenance and other operating charges w/o fuel, \$/MW hr		\$3.00	\$3.00	\$5.00	\$5.00	\$5.00	\$5.00
Characteristic plant cost, \$/KW		\$450	\$450	\$750	\$1,100	\$1,100	\$1,100
Ratio of fixed charges (capital, taxes and other) to plant cost (EIA 91)		7.3	7.3	7.3	7.3	7.3	7.3
Plant capacity factor, %		70%	70%	70%	70%	70%	70%
Fixed costs for a conventional plant, \$/MW hr		\$10.05	\$10.05	\$16.75	\$24.57	\$24.57	\$24.57
COE in \$/MW hr at char. eff. and plant cost		\$33.65	\$42.97	\$81.95	\$42.84	\$38.32	\$42.26
Target efficiency for a supercritical boiler, % HHV				45.0%	45.0%	45.1%	44.9%
Target capital cost for a supercritical boiler, \$/KW				\$850	\$1,200	\$1,200	\$1,200
COE for supercritical boiler				\$67.83	\$41.64	\$38.30	\$41.20
Target efficiency for advanced power system, % HHV				47.0%	47.0%	47.1%	46.9%
Target capital cost for advanced power system, \$/KW				\$850	\$900	\$900	\$900
COE for advanced power system				\$65.96	\$34.52	\$31.32	\$34.10
Impact of an Energy Tax of \$100		per Ton of Carbon					
Increase in fuel cost, \$/unit		\$1.57	\$0.17	\$12.89	\$71.65	\$77.97	\$65.44
Increase in energy cost, \$/MM Btu HHV		\$1.58	\$1.90	\$2.13	\$2.79	\$2.79	\$2.66
Increase in \$/MW hr at characteristic efficiency		\$10.81	\$12.96	\$22.17	\$28.55	\$28.41	\$27.30
Cost of fuel plus tax at characteristic efficiency, \$/MW hr		\$31.41	\$42.87	\$82.37	\$41.82	\$37.16	\$39.99
COE with carbon tax at characteristic efficiency		\$44.46	\$55.92	\$104.12	\$71.39	\$66.73	\$69.56
COE with tax for advanced systems		\$39.23	\$48.78	\$81.43	\$54.79	\$51.51	\$53.00

Figure 8. Cost estimate calculation.

$$H \frac{Btu}{lbmol} = A + B \times T(K) + \frac{C \times T(K)^2}{1000} + \frac{D \times T(K)^3}{10^6} + \frac{E \times T(K)^4}{10^9} + \frac{F \times T(K)^5}{10^{13}} + \frac{G \times 10^5}{T(K)} + \frac{H \times 10^7}{T(K)^2}$$

Figure 9. Equation format used for regression analysis of enthalpy data.

TABLE 3

Chemical Components Used in Regression Analysis of Enthalpy Data

Component	Source	Regression Range, °F
CO ₂	JANAF, 1985	-279 to 4041
CO	JANAF, 1985	-279 to 4041
N ₂	JANAF, 1985	-279 to 4041
O ₂	JANAF, 1985	-279 to 4041
NO ₂	JANAF, 1971	-279 to 4041
NO	JANAF, 1985	-279 to 4041
N ₂ O	JANAF, 1971	-279 to 4041
H ₂ O	JANAF, 1985	-279 to 4041
SO ₂	JANAF, 1985	-99 to 4041
SO ₃	JANAF, 1985	-99 to 4041
MgO	JANAF, 1985	-279 to 4041
MgCO ₃	JANAF, 1985	-279 to 1341
CH ₄	JANAF, 1985	-279 to 4041
H ₂	JANAF, 1985	-279 to 4041
H ₂ S	JANAF, 1985	-99 to 4041
NH ₃	JANAF, 1985	-279 to 4041
C ₃ H ₈	JANAF, 1985	32 to 1400
Fe ₂ O ₃ (I)	JANAF, 1985	-279 to 1251
Fe ₂ O ₃ (II and III)	JANAF, 1985	1251 to 4041
Water (liq.)	JANAF, 1985	45 to 441
Sulfur (s, alpha)	JANAF, 1985	-459 to 204
Pyrite, FeS ₂	JANAF, 1985	-279 to 2061
SiO ₂ (quartz)	JANAF, 1985	-279 to 1065
Al ₂ O ₃ (s)	JANAF, 1985	-99 to 3799

Continued . . .

TABLE 3 (continued)

Component	Source	Regression Range, °F
S ₂ (g)	JANAF, 1985	–279 to 4041
COS (g)	JANAF, 1985	–279 to 4041
CaO (s)	JANAF, 1985	–279 to 4041
CaCl ₂ (s)	JANAF, 1971	–99 to 3141
CaCl ₂ (liq)	JANAF, 1985	700 to 4041
Ca(OH) ₂ (s)	JANAF, 1985	–99 to 1341
CaS (s)	JANAF, 1985	–99 to 4041
Na ₂ O (gamma and beta s)	JANAF, 1985	–99 to 1778
Na ₂ O (alpha s and liq)	JANAF, 1985	1778 to 3141
NaOH (s)	JANAF, 1985	–459 to 570
NaCl (s)	JANAF, 1985	–279 to 1472
Na ₂ CO ₃ (s)	JANAF, 1985	–279 to 842
Na ₂ S (s)	JANAF, 1985	77 to 1837
Na ₂ SO ₄ (s)	JANAF, 1985	–279 to 1341
K ₂ O (s)	JANAF, 1985	77 to 3141
KCl (s)	JANAF, 1985	–279 to 2241
K ₂ S (s)	JANAF, 1985	77 to 1341
K ₂ SO ₄ (s)	JANAF, 1985	–279 to 1083
Carbon (s)	JANAF, 1985	–99 to 4941

STATEMENT OF WORK FOR ACTIVITY 3–ADVANCED FUEL CHARACTERIZATION

Activity 3 – Goals and Objectives

The EERC has installed state-of-the-art computer-controlled scanning electron microscopes and associated microanalysis systems. The image analysis capabilities and improved x-ray analysis systems associated with SEMs provide an opportunity to improve the overall CCSEM procedure to determine the size, composition, abundance, and association of inorganic components associated with fuels and combustion products. Improvements in backscattered electron imaging as well as image analysis capabilities provide an enhanced ability to distinguish between coal, mineral grains, and mounting media using automated procedures, and with improved x-ray detectors, the amount of inorganic elements associated with the organic matrix of the coal particles can be determined.

Activity 3 – Methods and Results

NMARL Analytical Accomplishments

The Natural Materials Analytical Research Laboratory (NMARL) focused on improving analytical techniques developed for the SEM. The techniques were originally developed for older SEMs which lacked the ability to do detailed image analyses, complete automation, and rapid calculations. Improvements in SEMs and integration with computers allow many improvements and upgrades of the older techniques to take advantage of much faster computers and sophisticated software. The analytical techniques that were improved are the point count (SEMPC) and the CCSEM methods.

Improvements to SEMPC

The SEMPC technique is an automated SEM technique used primarily for boiler tube deposit analyses where 250 point analyses are taken on a cross-sectional surface of the deposit or any other massive sample. Two modifications were made to this technique. In the past, the 250 chemical point analyses were done “blind,” meaning that there was no way of knowing if the beam was striking the sample of interest or the mounting medium. To compensate for this, analyses were stopped after 10 seconds of x-ray collection, and the spectrum was analyzed for chlorine and total counts. The presence of chlorine indicates that the point of analysis is missing any particles and is hitting the epoxy resin, which is the mounting medium for the sample. Low total x-ray counts indicate the beam is striking a pore where any x-rays that are generated cannot escape.

While eliminating any chlorine-containing analyses is acceptable for boiler tube deposits because of the temperatures at which they form, several other types of massive samples could potentially contain chlorine-containing salts, such as halite (NaCl). Also, the efficiency of the procedure is reduced by starting and stopping all analyses.

The first modification to the SEMPC technique was to change the way the spots for analyses were selected based on an image of a small section of the sample. The improved imaging of the SEM and image analysis capabilities of the analytical system would allow for more coal information, with the coal particles being identified as coal particles and sized, and then mineral inclusions identified, sized, and their density determined. A backscattered electron image (BEI) is collected which is an image of the sample generated from the electrons being bounced off of the surface of the sample. Heavier elements (higher atomic number) are generally larger and are capable of bouncing more electron off than lighter elements can. As a result, the grey-scale indicates chemical composition, with the light element compounds such as the epoxy mounting medium being very dark grey to black and the heavier element compounds being light grey to white. Pores or holes in the sample also tend to be dark by not allowing as many x-rays to escape back to the detector. Point analyses are then restricted to the light grey areas by the operator setting video thresholds to avoid epoxy analyses and pores. Since chlorine-containing epoxy can be avoided by this method, any compound that may contain chlorine can now be analyzed.

The second modification, still in progress, is a direct result of being able to select the points of analysis by imaging. The image analysis capabilities of a BEI can be subdivided into various grey-scale ranges that can be analyzed separately. Since the grey-scale intensity is dependent on the chemistry of the particle, it is possible to map chemically similar areas that can also be related to the viscosity of that compound at temperature.

The range of grey levels in a backscattered image is from 0 (black) to 255 (white). Any range between 0 and 255 can be selected and a binary image created using just those pixels in the image that fall in that range. Figure 10 shows a BEI and seven different grey-scale images (GS1–GS7) of a high-temperature deposit. GS1 (grey scale 1) is created to determine the total area of the deposit. The white area in GS1 represents the epoxy or sample-mounting medium, and the black area represents the deposit. The white areas represent those pixels having an intensity value between 0 and 120. Since exact pixel dimensions and number of pixels used to create the image are known, a simple calculation computes the cross-sectional area of the deposit in the frame. After many such frames, good information on the porosity of the deposit can be gained. GS2 is the darkest grey image, with the pixel intensities between 121 and 150. In this case, it is nearly confined to the deposit edges. GS3 is defined as those pixels with intensity values between 151 and 175; GS4 has pixel values between 176 and 200, GS5 between 201 and 230, GS6 between 231 and 250, and GS7 as those pixels between 251 and 255.

Each GS image is then analyzed, and the number of pixels in that grey image is used to calculate the area represented by those chemical compounds that correspond to that grey intensity range. The chemical compositions are determined for several areas in each binary image, and the viscosity of the liquid phase is calculated.

Figure 10. Grey scales used to determine phases.

Figure 11 shows the frequency distribution for the grey-scale images in different viscosity bins. Each grey-scale frequency show a bell-like curve with the lower the atomic number, the higher the viscosity. For example, the frequency distribution of GS2 peaks at about 4 $\log_{10}$ poise; GS4 peaks at around 3 $\log_{10}$ poise; and GS6 peaks at about 1 $\log_{10}$ poise.

Modifications to CCSEM

An automated technique is being developed to either enhance or replace the current chemical fractionation technique. This procedure is being incorporated into the current CCSEM program that will then include size, shape, and chemical data for the minerals associated with the coal and the inorganic constituents that are part of the coal matrix. The procedure is done at a magnification of 250 $\times$ and covers the entire sample, collecting chemical data from those coal particles larger than 4.6 μm . This size cutoff was selected to avoid analyzing charging effects in the mounting medium.

Table 4 shows a comparison of the elements measured in the coal particles in the column SEM EDS (energy-dispersive spectrometry) with the four XRF techniques of measurement. The first XRF technique is measured after low-temperature ashing (750 $^{\circ}\text{C}$), the second after being leached in water to remove any soluble salts, the third after leaching in ammonium acetate to remove the organically associated elements, and the fourth after being leached in hydrochloric acid to remove any carbonate material.

The SEM EDS method shows slightly higher Na and Ca and slightly lower Si than measured by the XRF methods. The SEM EDS method for this data set is based on approximately 750 data points, and work is in progress to determine if this is a sufficient number of point analyses for reproducible results.

Figure 11. Frequency distribution for grey-scale images.

TABLE 4

Comparison of Values (wt%) of the SEM and XRF Methods					
Element	SEM EDS	XRF-Init	XRF-H ₂ O	XRF-NH ₄ Ac	XRF-HCl
Na	0.21	0.04	0.04	0	0
Mg	0.35	0.2	0.2	0.04	0.01
Al	0.48	0.43	0.44	0.44	0.25
Si	0.15	0.55	0.55	0.55	0.55
P	0.03	0.02	0.02	0.02	0
S	0.54	0.35	0.29	0.26	0.01
Cl	0.1	0.03	0.04	0	0
K	0.09	0.01	0.01	0	0
Ca	2.11	1.25	1.26	0.44	0.02
Fe	0.42	0.31	0.31	0.29	0.06
Ba	0.09	0.03	0.04	0.01	0
Ti	0.07	0.05	0.05	0.05	0.04

Other modifications to the CCSEM procedure include the evaluation of the mineral binning categories. The older equipment was not capable of rapid ZAF correction. These are factors that influence spectrum differences between elements in pure form and elements in a compound. The NMARL uses ZAF correction to adjust for these factors. These calculations can now be done very rapidly with the now much faster computers. The corrected data are more reliable with all of these factors taken into account. This is especially important for light elements in heavier matrices.

The refinements to the mineral categories are being evaluated with the aid of multivariate analysis of the output generated by the CCSEM process. The multivariate analysis used is cluster analysis and is being done using Minitab® Release 13 software. Small adjustments will be made to the chemical criteria contained in an EERC Fortran program made specifically to categorize chemical analyses to mineral phases.

STATEMENT OF WORK FOR ACTIVITY 4 – SLAG FLOW BEHAVIOR

Activity 4 – Goals and Objectives

The properties of slags are also of importance in the performance of conventional and advanced power systems, with the temperature dependence of slag viscosity affecting slag flow (i.e., slag-tapping ability in cyclone-fired systems) and ash removability and producing undesirable deposition and corrosion issues. An improved method of predicting viscosity and the temperature

of critical viscosity is needed to adequately predict basic ash behavior, which is crucial in developing more sophisticated boiler performance models.

The goal of this activity was to provide improved predictions of slag viscosity and critical crystallization temperatures for a representative PRB subbituminous and a lignite coal. The specific objectives were to 1) perform a focused review of the literature models which addresses the temperature of critical viscosity, 2) perform equilibrium thermodynamic modeling of selected coal compositions to predict solid and liquid phases present as a function of temperature, and 3) use the calculations in conjunction with existing viscosity information and a few carefully selected high-temperature x-ray diffraction (HT-XRD) measurements to formulate an improved model for the prediction of viscosity and critical temperatures for these coals.

Activity 4 – Methods

Viscosity Measurement Protocol

Although a volume of viscosity measurement data was available from past projects, much of the data were suspect, since the measurements were performed using ceramic alumina crucibles to contain the slag, in spite of earlier work that demonstrated unequivocally that subbituminous and lignite slags leach alumina from the crucible, resulting in a significantly altered slag composition (9). In addition, most of the measurements were performed either in air or in a strongly reducing atmosphere simulating gasification conditions. In conjunction with other projects, a viscosity measurement protocol was developed and gas atmospheres selected which are designed to closely simulate the oxidizing and reducing conditions encountered in the barrel of a cyclone-fired boiler. Experimental viscosity data from several projects using the following procedures were then evaluated.

Sample Preparation

The samples were first ashed at 750°C in air to remove all combustible materials. Slags were then prepared by melting the ash or ash blend in a platinum crucible at 1500°C in air and then pouring the molten slag onto a room temperature brass plate to quench it. The slags were then crushed for placement in a crucible for viscosity testing.

Rotating-bob viscometer viscosities were measured with a Haake Viscometer 7 VT550 system equipped with a rotating-bob viscometer, shown in Figure 12. The bob is submerged into the slag until the slag just covers its top and is rotated at 45.3 rpm. The bob is 9 mm (0.354") in diameter and 20 mm (0.787") long with a 45 degree taper at each end. The torque required to rotate the bob is converted to an electrical signal which is then recorded and subsequently entered into a data reduction program that calculates the viscosity of the slag. The viscosity of the slags was normally measured over the range of 10 to 1000 poise unless crystallization was seen to occur along the walls of the crucible, at which point the measurements were terminated. The viscometer calibration of torque to viscosity is done using National Bureau of Standards silicate glass 710a with a known viscosity–temperature relationship.

Figure 12. Haake Viscometer 7 VT550 system equipped with a rotating-bob viscometer.

The rotating-bob viscometer consists of a box-type furnace with cylindrical holes aligned from the top to the bottom. An alumina tube is inserted through both holes, with the ends of the tube extending outside the furnace. The tube exiting out the bottom of the furnace is sealed with a cap. This is designed to prevent outside gases from entering, as well as to minimize escape of the test gas mixture from the furnace tube. A crucible containing approximately 50 g of slag is placed on a platform inside the alumina tube in the heated furnace section. The rotating bob is submerged in the molten slag with the shaft extending out the top of the alumina tube to the driving motor. A split loose-fitting cap at the top of the tube further minimizes gas exchange, while not affecting the shaft rotation.

Oxidizing and Reducing Atmospheres

The tests under oxidizing conditions were performed in a gas environment of 3.0% O₂, 14.0% CO₂, 0.10% SO₂, 10.0% H₂O, and 72.9% N₂. Tests under reducing conditions were performed in an atmosphere of 5% CO, 9% CO₂, 0.05% H₂S, 0.05% SO₂, 10% H₂O, and 75.9% N₂. Both oxidizing and reducing gas mixtures were introduced at a flow rate of 2.36 dm³/min (0.083 ft³/min). A steam generator was used to supply the H₂O. Cylinder gas compositions and flow rates were selected to maintain the final gas composition specified for the oxidizing and reducing atmospheres.

Crucible and Bob Materials

Viscosity testing under oxidizing conditions is generally standardized and straightforward. Platinum and platinum alloys have been found to be suitable unless significant metallic iron is

present. Metallic iron readily forms a low melting alloy with platinum, effectively dissolving it. The viscosity tests conducted under oxidizing conditions were performed using a pure platinum rod and bob and a 90% platinum/10% rhodium crucible. The rhodium alloy imparts greater rigidity and mechanical strength to the crucible without affecting the temperature and chemical resistance of the platinum.

Although platinum is unsuitable as a crucible material under strongly reducing conditions ($\text{CO}_2/\text{CO}/\text{H}_2$ gasifier atmospheres), because of attack by reduced metallic iron and metallic silicon, mildly reducing gas used for the current testing does not allow these species to form. Viscosity testing of the slags under reducing conditions has been performed using the same 90% platinum/10% rhodium crucible material as the oxidizing viscosity tests.

HS-XRD Measurements

X-ray diffraction measurements were performed using a Phillips X-Pert HT-XRD system equipped with a Buehler heated-stage chamber. The samples were heated in air on a Pt/Rd heated sample strip, with diffraction measurements performed both as the solid slag sample was heated to the point of being a molten liquid and then as the sample was cooled to ambient temperature.

Equilibrium Thermodynamic Calculations

The FACT code (10) was used to predict 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 by 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 analyses 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 an excess air level matching that of the gas composition used for experimental viscosity measurements under oxidizing conditions (3% O_2). A second similar calculation was performed to determine the amount of air required for combustion at near zero excess air (0.001% O_2) to roughly simulate reducing conditions. Since the gas composition for the experimental reducing conditions is not actually at equilibrium, FACT equilibrium calculations force significant changes in the major gas species, particularly CO and CO_2 , as a function of temperature.

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, this is for convenience as FACT determines the equilibrium amounts of gas, liquid, and solid compounds as a function of temperature based only on the amounts 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 which may not be kinetically or physically achieved. The compounds considered were approximately 30 major and minor gas species of highest concentration (FACT needs about this many gas species to allow the matrices to converge), a silicate-based liquid slag which is noted as SlagC, an iron-based liquid magnetite slag noted as Magn which is primarily important at high temperatures relating to liquid slag flow, a solid Ca–Mg sulfate solution, SCMO, which is indicative of potential low-temperature calcium-based fouling, and all pure solid species in the FACT database.

The calculations were performed on a weight basis to determine the percentage of liquid phases [(SlagC + Magn + liquid solution)/(all liquid + 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 (SlagC and Magn) as a function of temperature were then calculated using the Kalmanovitch-modified Urbain equation for each sample.

Calculation of Slag Viscosity

Slag viscosities were calculated using the Kalmanovitch-modified Urbain model (11) based on either the bulk ash composition or on the composition of liquid-phase material predicted by FACT. Calculations were performed at 25 °C intervals from 1500 °C to a temperature below the expected slag freezing points, 500 °C. Note that this model does not take oxidizing or reducing gas composition into account.

Activity 4 – Results

Literature Survey

A focused literature survey was made to determine the current state of viscosity modeling related to combustion systems, along with similar current experimental and modeling work being performed for mineralogical systems.

Temperature of Critical Viscosity

No new method for predicting the temperature of critical viscosity, T_{cv} , was found in the literature. The only work addressing T_{cv} remains the initial relationships proposed by Sage and McIlroy (12) and Hoy et al. (13). Neither of these models allows prediction of T_{cv} with any degree of confidence.

Viscosity Models

Several viscosity models have been developed, some for particular ranges of slag composition. These include:

- Sage–McIlroy Model (12)
- Hoy Model (13)

- Watt–Fereday Model (14)
- Bompkamp Modified Watt–Fereday Model (15)
- Kalmanovitch Modified Urbain Model (11)
- Schobert Modified Urbain Model (16)
- Senior Modified Urbain Model (17)
- Laumb Model (18)

Besides the Kalmanovitch Modified Urbain Model, the models which seem to give the best predictions are the Sage–McIlroy Model and the Senior Modified Urbain Model. The Kalmanovitch model and the Sage–McIlroy model work best for slags high in silica and low in iron, while the Senior model gives better predictions for high-iron coals. The Laumb Model examines the slag composition and then produces a T_{250} value which is a weighted average of the Senior model, the Kalmanovitch model, and the Sage–McIlroy model, with the weighting based on the performance of each model for the slag composition.

The Urbain equation to calculate viscosity is a modified Arrhenius model using a statistical approach (19). The relationship of viscosity to temperature is given by:

$$\text{viscosity} = A \times T \exp [1000 \times B/T]$$

where A is a preexponential factor representing the mass of structural units, the potential energy barrier to rearrangement, and the molar entropy resulting from hole formation in the melt. B is a function of the potential energy barrier and molar enthalpy. In practice, A and B are determined by regression analysis of the measured viscosities as a function of temperature for a suite of representative melts. The formulation was originally developed to predict viscosities for metallurgical slags. This model was modified by Kalmanovitch and Frank using an extensive literature database on the viscosity of CaO–MgO–SiO₂–Al₂O₃ glasses to provide refined values for the A and B terms. Other modifications have been made by Senior to accommodate high-iron coals and by Schobert for use with low-rank lignites.

Slagging Indices

Probably the most well-known indicator is the base-to-acid (B/A) ratio which is defined as

$$\frac{B}{A} \text{ ratio} = \frac{\sum Fe_2O_3 + CaO + MgO + Na_2O}{\sum SiO_2 + Al_2O_3 + TiO_2}$$

where the values of the oxides are in weight percent (13).

The concept is that a “base” is a metal oxide such as CaO which can react with an acid such as SiO₂. SiO₂, Al₂O₃, and TiO₂ are considered to be acids, and Fe₂O₃, CaO, MgO, Na₂O, and K₂O considered to be bases. Increasing the B/A ratio generally results in decreased viscosity until a minimum viscosity is reached at a B/A ratio of 1.0. The B/A ratio was empirically formulated, but is actually soundly based, since the oxides considered as acids and bases correspond to the elements generally acting as viscosity-increasing network formers and viscosity-decreasing network modifiers,

respectively. The B/A ratio does provide a valid indication of relative slag flow performance, although no information as to actual values such as T_{250} or T_{cv} .

Several other empirical indicators have been proposed, the most common of which are described here. Reviews of various indices and ratios are given by Jung (20) and by Briers (21).

The silica ratio (SR) is defined as:

$$SR = 100 \times \frac{SiO_2}{SiO_2 + \text{equivalent } Fe_2O_3 + CaO + MgO}$$

where:

$$\text{equivalent } Fe_2O_3 = Fe_2O_3 + 1.11 FeO + 1.43 Fe^0$$

and the values of the oxides are in weight percent (22). Use of the silica ratio requires a knowledge of the amount of iron in each oxidation state, which is normally obtained by analysis of the slag. For the purposes of these calculations, the equivalent Fe_2O_3 is taken to be the value of Fe_2O_3 in the ash, with no Fe^{+2} and Fe^0 present. Higher slag viscosities correspond to larger values of the silica ratio.

The lignitic factor (LF) is defined as:

$$LF = \frac{CaO + MgO}{Fe_2O_3}$$

with the values of the oxides in weight percent (23). An increase in the lignitic factor corresponds to higher viscosities.

The dolomite percentage (DP) is defined as:

$$DP = 100 \times \frac{CaO + MgO}{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}$$

with the values of the oxides in weight percent (23). Higher dolomite percentages tend to raise ash viscosity.

The slagging R_s index is defined as (24):

$$R_s = \frac{\frac{B}{A} \text{ ratio}}{\% S, \text{ on a dry basis}}$$

The R_s index was developed to indicate the potential severity of slagging. Values of < 0.6, 0.6–2.0, 2.0–2.6, and >2.6 correspond to low, medium, high, and severe slagging potential, respectively.

The iron-to-calcium (I/C) is defined as:

$$\frac{I}{C} = \frac{Fe_2O_3}{CaO}$$

with the values of the oxides in weight percent (25). Values of the I/C ratio between 0.3 and 3.0 correspond to low-viscosity eutectic mixtures. The I/C index was developed to indicate the potential severity of slagging.

Mineralogical Investigations

A substantial amount of experimental viscosity measurements on mineralogical systems has been published in the literature. Although not of the complexity of slags derived from coal ash, this data on pure minerals would be useful in providing additional verification of slag viscosity models. Although a detailed examination of the complete set of references was not undertaken, viscosity data is available on systems including alkali and alkaline-earth titanium silicate liquids (26), NaAlSiO₄–SiO₂ systems (27, 28), granitic melts (29), and anorthite (30). Although much of the work was performed at substantially elevated pressures, some information is available for near-ambient pressure conditions.

Three viscosity theories are in use to provide insight into mineralogical systems (31). The theories were specifically formulated to explain the phenomenon of glass transition, but also provide an expression of viscosity as a function of temperature. The free volume theory was developed in 1959 and subsequently modified. The basis of the model is that atoms are restricted to “cells” by adjacent atoms, with the cells solid or liquid depending on size. Atoms can diffuse when the excess volume is above a certain critical value. In equation form, a viscosity can be calculated as a function of temperature when four adjustable constants have been fitted to experimental viscosity data. The configurational entropy theory developed in 1958 relates the structural relaxation time of a liquid to the probabilities in configurational changes in the liquid. Viscosity can be calculated when two adjustable constants have been fitted with experimental viscosity data and the configurational entropy of the material experimentally measured calorimetrically. The mode coupling theory developed in 1984 uses the correlation of density fluctuations to determine the change in number density. Mode coupling is still being developed and *has yet to be applied to complex systems*. Both the free volume and configurational entropy models give quite good results for the mineral systems studied when fitted with the appropriate adjustable constants. They have the potential to be used in

coal-derived slag systems; however, there is a lack of experimental configurational entropy data for complex multicomponent systems.

The presence of water has a profound effect on viscosity in mineralogical systems. Examination of data by Hess and Dingwell (32) indicates that the presence of a few tenths of a percent of water will result in the lowering of viscosity by as much as an order of magnitude over the dry sample. Increasing levels of water continue to reduce viscosity, but less dramatically. This may be due to the water existing primarily as -OH groups at low water concentration, but the number of hydroxyl groups reaching a saturation point as the water level is increased (33). Since the slag viscosity measurements are carried out in a simulated combustion atmosphere containing 10% water vapor, the ability of slags to adsorb water and their water content is an area which should be further explored.

The basic model of silicate liquid viscosity is that of silica as a network former, forming -Si-O-Si- polymer chain and ring networks which increase slag viscosity. Cations such as Na⁺, Mg⁺⁺, and Ca⁺⁺ act as network modifiers, breaking the -Si-O-Si- bonds to produce smaller silicate network units, reducing viscosity. Evidence for actual atomic environments and element coordination numbers has been obtained in situ for magnesium (34), silicon (35), and oxygen (36) using high-temperature nuclear magnetic resonance (NMR) spectroscopy. Although the research is probably too fundamental to be applied to coal-derived slags, the availability of such a research tool should be kept in mind.

Slag Viscosity Measurements

The information which was assembled on experimental slag viscosity measurements from several projects included the following:

- A. Slag viscosity measurements on a suite of six subbituminous coals, two bituminous coals, three subbituminous-bituminous coal blends, and two bituminous coal-additive blends under both oxidizing and reducing conditions along with compositional data. Equilibrium thermodynamic modeling, viscosity modeling, and slag index calculations were performed on these samples. ASTM ash fusibility tests were also performed under oxidizing and reducing conditions for a majority of the samples.
- B. Slag viscosity measurements under oxidizing conditions on a suite of 19 lignite coal ashes and on slags from a full-scale utility boiler. Equilibrium thermodynamic modeling and viscosity modeling were performed on these samples.
- C. One slag viscosity measurement on a subbituminous coal under reducing conditions, with and without the addition of water.

In addition, data on two more suites of samples were obtained, but the results are not examined in detail in this report.

- D. Slag viscosity measurements on a bituminous coal and two bituminous coal–dolomite blends under oxidizing conditions, and on one bituminous coal–dolomite blend under reducing conditions. Equilibrium thermodynamic modeling and viscosity modeling were performed on these samples.
- E. Slag viscosity measurements under oxidizing conditions on a subbituminous coal and on three samples of the subbituminous coal ash blended with 10% addition of SiO_2 , Al_2O_3 , and CaO , respectively. Equilibrium thermodynamic modeling and viscosity modeling were performed on these samples.

Suite A Samples

Comparison of Experimental Viscosities, Models, and Slag Indices

Measurements of viscosity under oxidizing and reducing conditions were performed on the Suite A slag samples, along with ASTM ash fusibility tests. In addition, calculations were performed to predict the viscosity from bulk ash chemistry and viscosity and percentage of liquid-phase material using FACT calculations as a function of temperature.

The experimental slag viscosity measurements under oxidizing conditions give quite low viscosities, with T_{250} values below 1000°C for the subbituminous coals. The T_{250} values are higher for the bituminous coals, 1078°C , and an extremely high 1374°C for a high-silica coal. The blends of subbituminous and bituminous coals give intermediate viscosities, and the addition of additives to reduce viscosity has the desired effect.

The most striking result of the experimental slag viscosity measurements was the behavior under reducing conditions. With the exception of one bituminous slag–additive blend, the viscosities in the reducing gas atmosphere are the same as or higher than the viscosities under oxidizing conditions. The consistency of these results would indicate that this is not due to the uncertainties in the viscosity measurements. Higher reducing viscosities are seen for all but one of the subbituminous coals as well as one of the bituminous coals and one of the subbituminous–bituminous blends. These results are contrary to the accepted view that reducing conditions will result in lower slag viscosity as well as to the trends shown by the ASTM ash fusibility tests. It should be noted that the present measurements were performed under very mild reducing conditions and in the presence of 10% water vapor. Previous measurements made under reducing conditions at the EERC which show the expected lower viscosity have been performed under very strong reducing atmospheres containing approximately 30% hydrogen to simulate gasifier conditions, as has most reported literature measurements. Also, as detailed in the experimental section, the ASTM ash fusibility test is performed in a reducing CO/CO_2 atmosphere, but without the presence of water vapor. The use of a mildly reducing gas combined with water for the reducing viscosity measurements is probably unique. Previous results performed using ceramic crucibles showing an increase in viscosity under reducing conditions were ascribed to changes in slag composition due to interaction with the crucible material. However, the present results were obtained using inert platinum crucibles. The increase in viscosity under the mild reducing conditions seems to be the greatest for the subbituminous PRB coal slags. Four possible explanations are proposed:

1. The reducing conditions increase the volatility of sodium and potassium resulting in an altered slag composition of higher viscosity.
2. The presence of water vapor in combination with elements in the subbituminous slags enhances the formation of silicate polymer chain and ring structures resulting in increased viscosity.
3. The presence of water vapor under oxidizing conditions results in unexpectedly low viscosity values, and the presence of one or more of the reducing gases inhibits this effect.
4. Although they are dimensionally identical, the molybdenum bob used for the reducing viscosity measurements does not have the same viscosity calibration as the platinum bob.

Possibility No. 3 would explain why the calculated viscosities better match the experimental results under reducing conditions, as the coefficients used in the Kalmanovitch-modified Urbain equation were derived from experimental viscosity data on presumably dry glasses. Some evidence for increased slag viscosity for two slags as the result of the presence of water vapor under oxidizing conditions was previously reported by Folkedahl (37). In glasses, hydroxyl groups from water are expected to lower viscosity by acting as a modifier, which was not seen. It was suggested that the this might be the result of the presence of water enhancing crystallization.

An XRF analysis of one of the slags after the reducing viscosity measurement was performed suggested some depletion of sodium and potassium and that explanation No. 1 is possible. However, no corresponding analysis of the same slag sample after viscosity measurements under oxidizing conditions was available for comparison, and the comparison shown in Table 5 is based on the sulfur-free chemistry of the coal ash. Calculation of bulk viscosities for the two analyses indicated that the change in slag chemistry would have little effect on the viscosity, as shown in Figure 13.

The same slag was tested (Suite C) under reducing conditions with and without the addition of water vapor. This was an extended viscosity test, with the slag viscosity first measured in the presence of water vapor. The same slag sample was then immediately reheated in the viscometer and a second set of slag viscosity measurements made in the reducing gas atmosphere, but without water vapor being present. These results are shown in Figure 14. The first set of measurements served as a test of the reproducibility of the viscosity measurements. It should be noted that the slag for the Suite E tests was prepared from a second ASTM of the coal sample. It also shows that the viscosity measurements themselves have good reproducibility and that the high reducing condition viscosity is also reproducible. The second set of measurements showed no appreciable change in the viscosity when water vapor was not present. This would seem to rule out explanation No. 3. In retrospect, however, because the viscosity measurements were first made in the presence of water vapor, it is possible that the slag adsorbed water which remained present during the second set of viscosity measurements even though no water was present in the reducing gas mixture. Further investigation of the effect of water vapor on slag viscosity is needed to resolve this issue.

TABLE 5

Comparison of Ash and Slag Composition

Weight%	Subbituminous Coal		Difference
	Subbituminous Coal S-Free Ash Analysis	SEM Slag Analysis after Viscosity Measurement	
SiO ₂	32.22	36.61	4.39
Al ₂ O ₃	19.28	17.16	-2.12
Fe ₂ O ₃	7.78	9.18	1.40
TiO ₂	1.68	1.97	0.29
P ₂ O ₅	1.20	1.05	-0.15
CaO	28.14	28.53	0.39
MgO	7.43	3.94	-3.49
Na ₂ O	1.08	1.04	-0.04
K ₂ O	1.20	0.52	-0.68

Figure 13. Change in slag chemistry as it affects viscosity.

Figure 14. Slag sample showing viscosity measurements in a reducing gas atmosphere without water vapor after reheating in the viscometer.

Comparison of Experimental and Calculated Viscosities

The experimentally measured slag viscosities differ significantly from viscosities calculated using the Kalmanovitch-modified Urbain equation based on either the bulk ash viscosity or the composition of liquid-phase material predicted by FACT. A listing of experimental and calculated T_{250} and T_{80} temperatures (temperature at which the slag viscosity is 250 and 80 poise, respectively) is given in Table 6 along with experimental ash fusion temperatures and slagging index calculation results. In nearly all cases, the models predict a higher viscosity as a function of temperature than the experimental measurements. The calculated viscosities based on bulk ash composition also generally give lower values than do those based on the FACT calculations. Both model predictions do follow the experimental trend of increasing viscosity with decreasing temperature, but are offset to higher viscosity values. Two cases of viscosity values based on bulk composition which are significantly lower than the actual values occurred. As previously noted, the calculated values based on bulk composition are closer to the experimental values under reducing conditions. Although not predicting viscosity as a function of temperature, the Laumb calculation of the T_{250} temperature is generally closer to the actual value than either of the viscosity calculations.

The models do correctly predict trends in slag viscosity, although the calculated viscosities are generally offset to higher values than the experimental viscosities. Table 7 summarizes the correlations of a series of linear regressions comparing the experimental T_{80} and T_{250} temperatures with those calculated by the models. Both the Laumb and FACT calculations have fairly high r^2 values, indicating good correlation of the calculated temperatures with the experimental values.

TABLE 6

Comparison of Calculated Indices with Experimental Viscosities

	Subbituminous Coal	Subbituminous Coal	Bituminous Coal	Subbituminous– Bituminous Blend	Subbituminous– Bituminous Blend	Bituminous Coal	Bituminous Additive Blend
Base/Acid Ratio	0.66	1.71	0.45	1.15	0.68	0.22	0.35
Silica Ratio	53.56	25.99	66.83	37.20	53.78	84.19	72.77
Lignitic Factor	2.65	4.46	0.68	3.01	1.50	1.02	2.53
Dolomite Percentage	68.20	79.40	36.13	71.81	55.79	37.21	60.25
R _s	0.54	0.62	1.24	0.88	1.11	0.40	0.43
Iron/Calcium ratio	0.45	0.28	1.93	0.42	0.85	1.34	0.45
Comparison of T ₂₅₀ Values Temperature, °C							
Bulk Viscosity, predicted	1100	891	1238	975	1102	1498	902
Laumb, Bulk Viscosity, predicted	954	900	1294	983	1141	1529	1267
FACT, predicted	1125	1053	1295	1107	1154	>1500	1355
Oxidizing Viscosity, measured	876	<870	1078	948	1009	1374	1205
Reducing Viscosity, measured	979	963	1194	967	1045	1405	1222
Temperature, °F							
Bulk Viscosity, predicted	2012	1636	2260	1787	2016	2728	1656
Laumb, Bulk Viscosity, predicted	1749	1652	2361	1801	2086	2785	2313
FACT, predicted	2057	1927	2363	2025	2109	>2730	2471
Oxidizing Viscosity, measured	1609	<1600	1972	1738	1848	2505	2201
Reducing Viscosity, measured	1794	1765	2181	1773	1913	2561	2232
Comparison of T ₈₀ Values Temperature, °C							
Bulk Viscosity, predicted	1209	993	1352	1079	1212	>1500	1005
FACT, predicted	1284	1186	1392	1180	1285	>1500	1483
Oxidizing Viscosity, measured	965	888	1201	1014	1101	>1410	1341
Reducing Viscosity, measured	1121	995	1361	1065	1161	>1410	appr. 1410
Temperature, °F							
Bulk Viscosity, predicted	2208	1819	2466	1974	2214	>2730	1841
FACT, predicted	2343	2167	2538	2156	2345	>2730	2701
Oxidizing Viscosity, measured	1769	1630	2194	1857	2014	>2570	2446
Reducing Viscosity, measured	2050	1823	2482	1949	2122	>2570	2570

Base/Acid Ratio = 1 gives lowest viscosities

Silica Ratio = higher values give higher viscosities

Lignitic Factor = higher values give higher viscosities

Dolomite Percentage = higher values give higher viscosities

R_s = higher values give higher viscosities

Iron/Calcium Ratio = 0.3 to 3.0 give lowest viscosities

Continued . . .

TABLE 6 (continued)

	Bituminous Additive Blend	Subbituminous Coal	Subbituminous Coal No. 1	Subbituminous Coal No. 2	Subbituminous Coal	Subbituminous– Bituminous Blend
Base/Acid Ratio	0.66	1.71	0.45	1.15	0.68	0.22
Silica Ratio	53.56	25.99	66.83	37.20	53.78	84.19
Lignitic Factor	2.65	4.46	0.68	3.01	1.50	1.02
Dolomite Percentage	68.20	79.40	36.13	71.81	55.79	37.21
R _s	0.54	0.62	1.24	0.88	1.11	0.40
Iron/Calcium ratio	0.45	0.28	1.93	0.42	0.85	1.34
Comparison of T ₂₅₀ Values Temperature, °C						
Bulk Viscosity, predicted	1100	891	1238	975	1102	1498
Laumb, Bulk Viscosity, predicted	954	900	1294	983	1141	1529
FACT, predicted	1125	1053	1295	1107	1154	>1500
Oxidizing Viscosity, measured	876	<870	1078	948	1009	1374
Reducing Viscosity, measured	979	963	1194	967	1045	1405
Temperature, °F						
Bulk Viscosity, predicted	2012	1636	2260	1787	2016	2728
Laumb, Bulk Viscosity, predicted	1749	1652	2361	1801	2086	2785
FACT, predicted	2057	1927	2363	2025	2109	>2730
Oxidizing Viscosity, measured	1609	<1600	1972	1738	1848	2505
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Bulk Viscosity, predicted	1209	993	1352	1079	1212	>1500
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Lignitic Factor = higher values give higher viscosities

Dolomite Percentage = higher values give higher viscosities

R_s = higher values give higher viscosities

Iron/Calcium Ratio = 0.3 to 3.0 give lowest viscosities

TABLE 7

Regression Analysis of Models and Predictive Indices		
$[\text{calculated } T_{250}] = m [\text{experimental } T_{250}] + b$		
$r^2 = \text{Correlation Coefficient}$		
Temperatures are in °C		
VISCOSITY MODELS		
Calculated	Experimental T_{250} (oxidizing) r^2	Experimental T_{250} (reducing) r^2
Bulk Viscosity T_{250}	0.378	0.342
Laumb T_{250}	0.845	0.716
FACT T_{250}	0.868	0.779
Calculated	Experimental T_{80} (oxidizing) r^2	Experimental T_{80} (reducing) r^2
Bulk Viscosity T_{250}	0.225	0.169
FACT T_{250}	0.812	0.820
VALUES WITH TWO OUTLYING VISCOSITY VALUES REMOVED		
Calculated	Experimental T_{250} (oxidizing) r^2	Experimental T_{250} (reducing) r^2
Bulk Viscosity T_{250}	0.854	0.418
Laumb T_{250}	0.853	0.728
FACT T_{250}	0.852	0.792
VALUES WITH TWO OUTLYING VISCOSITY VALUES REMOVED		
Calculated	Experimental T_{80} (oxidizing) r^2	Experimental T_{80} (reducing) r^2
Bulk Viscosity T_{250}	0.788	0.283
FACT T_{250}	0.751	0.849

Continued . . .

TABLE 7 (continued)

$$[\text{calculated } T_{250}] = m [\text{experimental } T_{250}] + b$$

 r^2 = Correlation Coefficient

Temperatures are in °C

ASH FUSION		
Oxidizing Conditions	Experimental T_{250} (oxidizing)	Experimental T_{250} (reducing)
	r^2	r^2
Initial Temperature	0.14	0.259
Softening Temp.	0.339	0.495
Hemispherical Temp.	0.352	0.467
Fluid Temp.	0.628	0.678
Reducing Conditions	Experimental T_{250} (oxidizing)	Experimental T_{250} (reducing)
	r^2	r^2
Initial Temp.	0.293	0.445
Softening Temp.	0.352	0.490
Hemispherical Temp.	0.386	0.510
Fluid Temp.	0.493	0.598
Oxidizing Conditions	Experimental T_{80} (oxidizing)	Experimental T_{80} (reducing)
	r^2	r^2
Initial Temp.	0.134	0.347
Softening Temp.	0.300	0.471
Hemispherical Temp.	0.316	0.501
Fluid Temp.	0.654	0.812
Reducing Conditions	Experimental T_{80} (oxidizing)	Experimental T_{80} (reducing)
	r^2	r^2
Initial Temp.	0.319	0.474
Softening Temp.	0.370	0.512
Hemispherical Temp.	0.427	0.634
Fluid Temp.	0.486	0.617

Continued . . .

TABLE 7 (continued)

[calculated T_{250}] = m [experimental T_{250}] + b		
r^2 = Correlation Coefficient		
Temperatures are in °C		
SLAG INDICES		
	Experimental T_{250} (oxidizing) r^2	Experimental T_{250} (reducing) r^2
Base/acid Ratio	0.275	0.524
Silica Ratio	0.771	0.722
Lignitic Factor	0.311	0.181
Dolomite Percentage	0.381	0.240
R_s	0.000	0.001
Iron/Calcium Ratio	0.122	0.028
1/[Base/Acid Ratio]	0.903	0.924
	Experimental T_{80} (oxidizing) r^2	Experimental T_{80} (reducing) r^2
Base/Acid Ratio	0.631	0.769
Silica Ratio	0.780	0.850
Lignitic Factor	0.263	0.276
Dolomite Percentage	0.314	0.352
R_s	0.001	0.001
Iron/Calcium Ratio	0.077	0.098
1/[Base/Acid Ratio]	0.848	0.741

However, the calculations using the bulk viscosity show a much poorer correlation. As noted, viscosity values based on bulk composition were significantly lower than the actual values for two of the slags. Regressions performed with these two data points removed result in bulk viscosity r^2 values comparable to those for the Laumb and FACT models.

The Laumb model appears to give the best estimate of T_{250} , and the viscosity calculation based on bulk ash chemistry gives a better fit to the experimental measurements than the viscosity based on the FACT calculations. However, these methods predict T_{250} values averaging approximately 100° and 140°C from the experimental T_{250} values, with quite large deviations for individual slags. The three models (with the two anomalous data points removed from the bulk viscosity calculation) successfully predict trends consistent with measured viscosity values with a good correlation between measured and calculated T_{250} and T_{80} values, although the actual values differ from those measured.

The prediction by FACT of slag liquid phases for the Suite A samples in general did not correlate well to the experimental viscosity measurements. In some cases, a decrease in the percentage of liquid phases (indicating the formation of solid crystals) does appear to coincide with

abrupt increases in experimental viscosity. However, in many cases, the change in the calculated percentage of liquid phases is not reflected in the experimental behavior. The viscosity calculated from the liquid-phase composition also does not predict experimental viscosity measurements as well as the calculations based on simple bulk viscosity.

Comparison of Experimental Viscosities with Ash Fusibility Measurements

Comparison of the ASTM ash fusibility results (initial, softening, hemispherical, and fluid temperatures) with the experimental viscosity curves revealed no obvious relationship between these temperatures and actual viscosity behavior or T_{250} . There is the expected trend, of course, of more viscous slags having higher fusibility temperature values. A series of linear regressions were performed to determine if correlations existed between experimental T_{250} and T_{80} temperatures and the four ash fusibility temperatures, the results of which are given in Table 7. Surprisingly, reasonably good r^2 values for the fusibility fluid temperature under oxidizing conditions along with the initial and softening temperatures under reducing conditions were found. This would indicate that the fusibility temperatures have some relationship to the slag viscosity, but do not correspond to the actual T_{250} and T_{80} values. Due to the small dataset used for the regression analysis, these correlations may be coincidental.

Comparison of Experimental Viscosities with Slagging Indices

Also given in Table 7 are the results of linear regression analyses comparing experimental T_{250} and T_{80} values with the calculated slagging index values given in Table 6. The only slagging indices with r^2 values suggesting any reasonable correlation with experimental viscosity measurements are the base/acid ratio and the silica ratio. This is reasonable, since these two index calculations reflect a simple accounting of silica network formers and modifiers analogous to the viscosity models. Examination of plotted base/acid ratios versus T_{250} and T_{80} temperatures suggested a possible inverse relationship. Accordingly, a regression analysis was also performed using values of $1/(\text{base/acid ratio})$ (or acid/base ratio). Surprisingly, this regression analysis using $1/(\text{base/acid ratio})$ gave r^2 values higher than those for the more sophisticated viscosity model predictions. Again, due to the small size of the dataset, this high correlation may be coincidental.

Suite B Samples

Comparison of Experimental and Calculated Viscosities

Slag viscosity measurements were performed under oxidizing conditions on 18 lignite coal ash samples and on one slag sample from a full-scale utility boiler. Equilibrium thermodynamic modeling and viscosity modeling were performed on these samples. A comparison of T_{80} and T_{250} values for these samples is given in Table 8.

Viscosities calculated both from the FACT modeling and from the bulk ash chemistry predict viscosities similar to, but generally somewhat higher than, the experimental viscosity measurements. As with the Suite A samples, the viscosity predicted by FACT is higher than that predicted from the bulk ash chemistry. The calculated viscosity curves follow the general trend of the experimental values. An example is shown for one of the samples in Figure 15. The average absolute difference

TABLE 8

Summary of Suite B Experimental and Calculated T_{250} and T_{80} Values

Material	<u>Experimental</u>		<u>FACT</u>		<u>Bulk</u>	
	$T_{250}, ^\circ\text{C}$	$T_{80}, ^\circ\text{C}$	$T_{250}, ^\circ\text{C}$	$T_{80}, ^\circ\text{C}$	$T_{250}, ^\circ\text{C}$	$T_{80}, ^\circ\text{C}$
Lignite	968	964	1142	1251	1010	1115
Lignite	1437	NA	1478	NA	1415	NA
Lignite	858	908	1034	1243	962	1067
Slag	1192	1262	1188	1262	1123	1233
Lignite	943	974	1025	1087	937	1040
Lignite	1126	1207	1163	1261	1062	1170
Lignite	1068	1139	1298	1425	1225	1337
Lignite	968	1081	1269	1372	1180	1292
Lignite	896	975	1186	1262	1053	1162
Lignite	936	1058	1242	1274	1087	1197
Lignite	1046	1201	1263	1332	1155	1264
Lignite	899	992	1270	1367	1184	1295
Lignite	1023	1198	1265	1334	1142	1252
Lignite	1058	1275	1269	1367	1182	1294
Lignite	997	1028	1163	1254	979	1083
Lignite	903	978	1117	1224	1025	1131
Lignite	985	1121	1260	1320	1132	1242
Lignite	1108	1261	1341	1467	1267	1379
Lignite	937	1041	1211	1270	1075	1184
Lignite	1093	1241	1298	1425	1225	1337

Absolute Differences

	Average	Std. Dev.	Min.	Max.
FACT T_{250}	202.45	104.83	0	371
FACT T_{80}	204.89	105.80	0	375
Bulk T_{250}	116.85	70.76	0	285
Bulk T_{80}	121.16	76.58	0	303

Figure 15. Predicted versus measured viscosity.

between the experimental and predicted T_{80} and T_{250} values in the table was approximately 200°C for the FACT model and 120°C using the bulk ash chemistry. Both prediction methods exhibited large standard deviations as well, so that the discrepancy between actual and predicted viscosity could be substantial for a given slag. Calculation of viscosity using the bulk ash chemistry is seen to result in closer agreement with experimental measurements than the FACT model.

The FACT results do indicate a precipitous decrease in the amount of liquid phases as well as a sharp increase in viscosity at approximately the same temperature as the experimental viscosity measurements were terminated because of freezing of the slags, an example of which is also shown in Figure 15. It should be noted that the predictions made by the FACT model are dependent on the liquid and solid species selected for the calculation, as well as on the species available in the FACT database. It is expected that refinement of the species used in the calculation would improve the correspondence of the FACT viscosity as well as the amount of solid phase predicted.

Comparison of HT-XRD Results with FACT Calculations

Based on viscosity behavior under oxidizing conditions, a lignite Suite B sample and a subbituminous Suite A sample were selected for examination by HT-XRD. The experimental oxidizing viscosity, the calculated FACT viscosity and percentage of liquid phases, and the calculated viscosity based on bulk composition are shown in Figures 16 and 17 for the lignite and subbituminous, respectively. The lignite slag exhibits a T_{cv} at approximately 1190°C, which is coincident with the T_{250} temperature of 1192°C. The subbituminous slag shows an apparent T_{cv} of approximately 925°C, with the slag freezing before a viscosity of 250 poise is reached. This slag also

Figure 16. Calculated viscosity comparisons for the lignite coal.

Figure 17. Viscosity calculations comparisons for the subbituminous coal.

exhibits long temperature regions of nearly constant viscosity, but with a small abrupt increase in viscosity between 1275° and 1300°C, followed by another small viscosity increase at 1100°C.

HT-XRD scans were performed on the samples in air, first as the temperature was increased until the slag became molten with no crystalline phases present, then cooled to record the appearance of solid phases. Scans were also performed at 30°, 250°, and 500°C during the heating and cooling cycle. Based on the experimental viscosities, a temperature of 750°C was selected as a starting point for the XRD scans which were then performed at 50°C temperature intervals. It should be noted that, because of the extremely small sample size and geometry, it is not possible to quantify the relative amounts of the solid crystalline phases detected by HT-XRD, nor can the presence of solid amorphous glasses be detected.

The crystalline phases detected by HT-XRD as a function of temperature for the two slags on heating and cooling are given in Tables 9 and 10. Some hysteresis is seen in the mineral behavior. For example, in the lignite slag, crystalline diopside disappears at 1100°C, but reappears on cooling at 1150°C. There are also some differences in the crystalline mineral phases present on heating versus those appearing as the liquid slag is cooled.

Figure 18 shows the experimental viscosity curve for the lignite slag plotted with the crystalline mineral phases identified as the slag was cooled. The T_{cv} as well as the slag freezing point appear to coincide with the appearance of diopside $[Ca(Mg,Al)(Si,Al)_2O_6]$. A similar plot for the subbituminous slag is shown in Figure 19. The first small step increase in viscosity at 1275°C may correspond to the appearance of crystalline spinel, ferrian $[Mg(Al,Fe)_2O_4]$, and augite $[Ca(Fe,Mg)Si_2O_6]$. The second small step increase in viscosity at 1100°C may be related to the appearance of gehlenite $[Ca_2Al_2SiO_7]$. The T_{cv} and freezing point of the subbituminous slag appear to be related to the formation of crystalline maghemite $[Fe_2O_3]$ and $Ca_2Fe_9O_{13}$ (no common mineral name).

The solid species predicted by FACT as a function of temperature for the lignite slag are shown in Figure 20. No predicted solid phase appears at the experimental temperature of critical viscosity (1190°C), although Fe_2O_3 (hematite) and some $CaAl_2Si_2O_8$ (anorthite) are predicted to form at 1250° to 1300°C and some $Ca_3Fe_2Si_3O_{12}$ (andradite) at 1150°C. A sharp decrease in the total amount of liquid phases also occurs roughly around the T_{cv} temperature. The FACT calculations of solid species as a function of temperature for the subbituminous slag are shown in Figure 21. Here the total number of liquid species decreases to a low level (<20%) at a temperature well above the T_{cv} temperature. Although the amounts of solid species appear to be incorrect, $MgOCa_3O_3Si_2O_4$ (merwinite) is predicted to form at approximately the point of the first small increase in experimental viscosity (1275°C) and $CaFe_2O_4$ (no common mineral name) at the second small viscosity increase (1100°C). Somewhat below the T_{cv} point, $Ca_3Fe_2Si_3O_{12}$ (andradite) is predicted to form.

The solid mineral species as well as the total amount of liquid phases present predicted by FACT do not well match the experimental HT-XRD results. It is believed that three factors are responsible. Several of the species identified by XRD, such as diopside and plagioclase feldspar, represent a series of minerals with variable composition, for which the FACT database contains only the end members. A critical part of the FACT modeling is the selection of the liquid phase. This is

TABLE 9

HT-XRD Results for Lignite Slag

Temp., °C	Amorphous Glass	Fayalite Fe ₂ SiO ₄	Diopside Ca(Mg,Al)(Si,Al) ₂ O ₆	Ankermanite Ca ₂ MgSi ₂ O ₇	Hematite Fe ₂ O ₃	Plagioclase Feldspar Na(AlSi ₃ O ₈)– Ca(Al ₂ Si ₂ O ₈)	Liquid Melt
HEATING							
30	X						
250	X						
500		X		X	X	X	
750		X	X		X	X	
1000			X		X	X	
1050			X			X	
1100			X			X	
1150							X
1200							X
1250							X
1300							X
COOLING							
30		X	X		X	X	
250		X	X		X	X	
500		X	X			X	
750		X	X			X	
1000			X			X	
1050			NA			NA	
1100			X				
1150			X				
1200							X
1250							X
1300							X

TABLE 10A

HT-XRD Results for Subbituminous Slag

Temp., °C	Amorphous Glass	Ca ₂ Fe ₉ O ₁₃	Diopside Ca(Mg,Al)(Si,Al) ₂ O ₆	Augite Ca(Fe,Mg) Si ₂ O ₆	Ankermanite Ca ₂ MgSi ₂ O ₇	Gehlenite Ca ₂ Al ₂ SiO ₇	Hematite Fe ₂ O ₃	Maghemite Fe ₂ O ₃	Plagioclase Feldspar Na(AlSi ₃ O ₈)– Ca(Al ₂ Si ₂ O ₈)	Spinel, Ferrian Mg(Al,Fe) ₂ O ₄	Liquid Melt
HEATING											
30	X		X								
250	X		X								
500			X		X						
750		X	X		X						
800		X	X		X						
850		X	X		X						
900			X		X						
950			X		X		X				
1000			X		X		X		X		
1050			X		X		X		X		
1100			X		X		X				
1150			X		X						
1200			X		X						
1250			X								
1300											X
1350											X

TABLE 10B

HT–XRD Results for Subbituminous Slag

Temp., °C	Amorphous Glass	Ca ₂ Fe ₉ O ₁₃	Diopside Ca(Mg,Al)(Si,Al) ₂ O ₆	Augite Ca(Fe,Mg)Si ₂ O ₆	Ankermanite Ca ₂ MgSi ₂ O ₇	Gehlenite Ca ₂ Al ₂ SiO ₇	Hematite Fe ₂ O ₃	Maghemite Fe ₂ O ₃	Plagioclase Feldspar Na(AlSi ₃ O ₈)– Ca(Al ₂ Si ₂ O ₈)	Spinel, Ferrian Mg(Al,Fe) ₂ O ₄	Liquid Melt
COOLING											
30		X		X		X		X		X	
250		X		X		X		X		X	
500		X		X		X		X		X	
750		X		X		X		X		X	
800				X		X				X	
850				X		X				X	
900				X		X				X	
950				X		X				X	
1000				X		X				X	
1050				X						X	
1100				X						X	
1150				X						X	
1200				X						X	
1250											X
1300											X
1350											X

Figure 18. Experimental viscosity curve for the lignite slag plotted with the crystalline mineral phases identified as the slag was cooled.

Figure 19. Experimental viscosity curve for the subbituminous slag plotted with the crystalline mineral phases identified as the slag was cooled.

Figure 20. Solid species predicted by FACT as a function of temperature for the lignite slag.

Figure 21. Solid species predicted by FACT as a function of temperature for the subbituminous slag.

approximated with a liquid solution Slag-C in the FACT database which does not contain iron in the composition. Iron species are accounted for with a second liquid magnetite solution Magn from the FACT database. When the Magn liquid solution is no longer thermodynamically favored, the iron in the system must appear in the solid phases since there is no longer a liquid iron-containing solution. It is felt that this occurs at temperatures much higher than what actually occurs in the slag on cooling. Finally, the FACT calculations at each temperature are independent of each other; i.e., the change in composition due to the formation of solid material is not taken into account. Because of the difficulty of recalculating the amount and composition to account for solid species formation at each temperature, this has not yet been attempted.

Model Development

The ability to accurately predict slag viscosity as a function of temperature is seen as the first essential step before progress can be made to predict the temperature of critical viscosity. The Kalmanovitch-modified Urbain equation often gives temperatures for important viscosities, such as T_{250} , which diverge widely from experimental values.

The prediction of slag viscosity is complicated by the evidence from HT-XRD that the experimental viscosity measurements are being made on a two-phase system of liquid material and solid crystals. The measurements performed on the subbituminous slag detected the presence of crystalline phases forming in the slag melt well above the experimental T_{250} and freezing points of the slag. However, viscosity predictions may have to consider the rheological properties of a suspended solid in the slag, as well as the properties of the liquid slag itself. The viscosity of a two-phase mixture can be expressed as (38):

$$\text{viscosity}_{\text{mixture}} = \text{viscosity}_{\text{liquid}} (1 + 2.5 c + ac^2)$$

where:

c = volume concentration of solids and a = an interaction coefficient. The use of this equation for calculating the viscosity of liquid–solid slag mixtures depends on the ability of a thermodynamic equilibrium program such as FACT to predict the amount of solid phases present.

CONCLUSIONS

A focused literature survey indicated no new methodology for predicting the temperature of critical viscosity since the original relationships first proposed. Several models have been developed for calculating slag viscosity, some for particular composition ranges. Comparison of the Kalmanovitch-modified Urbain model and the Laumb model with experimental viscosity data indicated only fair correlation, often with wide differences in the predicted and measured viscosities. Other slagging index predictors were compiled and tested as well. The recent mineralogical literature was found to contain much useful information, including experimental viscosity data on mineral systems, the current state of theories on liquid silicate mineral systems, and the effect of water on liquid silicate mineral viscosity.

Measurements of viscosity under oxidizing and reducing conditions were performed on the slags produced from 13 Suite A samples. The most striking result of the experimental slag viscosity measurements was the behavior under reducing conditions, with the viscosities generally the same as or higher than the viscosities under oxidizing conditions. These results are contrary to the accepted view that reducing conditions will result in lower slag viscosity as well as to the trends shown by the ASTM ash fusibility tests. This may be the result of the use of a mildly reducing gas combined with water for the reducing viscosity measurements. Possible explanations are 1) that the reducing conditions increase the volatility of sodium and potassium resulting in an altered slag composition of higher viscosity; 2) that the presence of water vapor in combination with elements in the subbituminous slags enhances the formation of silicate polymer chain and ring structures resulting in increased viscosity; 3) that the presence of water vapor under oxidizing conditions results in unexpectedly low viscosity values, and the presence of one or more of the reducing gases inhibits this effect; or 4) that, although they are dimensionally identical, the molybdenum bob used for the reducing viscosity measurements does not have the same viscosity calibration as the platinum bob. An XRF analysis of one of the slags after the reducing viscosity measurement was performed suggested some depletion of sodium and potassium and that explanation No. 1 is possible. The same slag was tested under reducing conditions with and without the addition of water vapor. There was no appreciable change in the viscosity when water vapor was not present. This would seem to rule out explanation No. 3. In retrospect, however, because the viscosity measurements were first made in the presence of water vapor, it is possible that the slag adsorbed water which remained present during the second set of viscosity measurements even though no water was present in the reducing gas mixture. Further investigation of the effect of water vapor on slag viscosity is needed to resolve this issue.

The experimentally measured slag viscosities differ significantly from viscosities calculated using the Kalmanovitch-modified Urbain equation based on either the bulk ash viscosity or the composition of liquid-phase material predicted by FACT. In nearly all cases, the models predict a higher viscosity as a function of temperature than the experimental measurements. The calculated viscosities based on bulk ash composition also generally give lower values than do those based on the FACT calculations. Both model predictions do follow the experimental trend of increasing viscosity with decreasing temperature, but are offset to higher viscosity values. Although not predicting viscosity as a function of temperature, the Laumb calculation of the T_{250} temperature is generally closer to the actual value than either of the viscosity calculations. The models did correctly predict trends in slag viscosity although the calculated viscosities are generally offset to higher values than the experimental viscosities. The prediction by FACT of slag liquid phases for these slags in general did not correlate well to the experimental viscosity measurements. In some cases, a decrease in the percentage of liquid phases did appear to coincide with abrupt increases in experimental viscosity. However, in most cases, the change in the calculated percentage of liquid phases is not reflected in the experimental behavior.

Comparison of the ASTM ash fusibility results (initial, softening, hemispherical, and fluid temperatures) with the Suite A experimental viscosity curves revealed no obvious relationship between these temperatures and actual viscosity behavior or T_{250} . However, regression analysis indicated correlations existed between experimental T_{250} and T_{80} temperatures, and the fusibility fluid temperature under oxidizing conditions; and under reducing conditions, correlations also existed

with the initial and softening temperatures. This indicated that some relationship to the slag viscosity exists, but does not correspond to the actual T_{250} and T_{80} values.

Regression analyses comparing experimental T_{250} and T_{80} values for the Suite A slags with the calculated slagging index values indicated the only reasonable correlations with experimental viscosity measurements are given by the base/acid ratio and the silica ratio. The regression analysis using $1/(\text{base/acid ratio})$ showed a very good correlation, higher than those for the more sophisticated viscosity model predictions.

Viscosities calculated both from the FACT modeling and from the bulk ash chemistry for the 18 Suite B slags predict viscosities similar to, but generally somewhat higher than, the experimental viscosity measurements. As with the Suite A samples, the viscosity predicted by FACT is higher than that predicted from the bulk ash chemistry. The calculated viscosity curves follow the general trend of the experimental values, but the difference between experimental and predicted viscosity could be substantial for a given slag. The FACT results do indicate a precipitous decrease in the amount of liquid phases as well as a sharp increase in viscosity at approximately the same temperature as the experimental viscosity measurements were terminated because of freezing of the slags. It is expected that refinement of the species used in the calculation would improve the correspondence of the FACT viscosity as well as the amount of solid phase predicted.

HT-XRD measurements of a lignite and a subbituminous slag identified crystalline mineral phases appearing as the slag was cooled which corresponded quite closely with changes in experimental viscosity as well as the T_{cv} temperature and the slag freezing points. The solid species predicted by FACT as a function of temperature as well as the total amount of liquid phases present do not well match the experimental HT-XRD results. This is believed to be the result of species such as diopside and plagioclase feldspar with variable composition, for which the FACT database contains only the end members, the available selection of FACT liquid-phase solutions, and the difficulty of recalculating the liquid-phase composition to account for solid species formation at each temperature, which has not yet been attempted.

The prediction of slag viscosity by models such as the Kalmanovitch-modified Urbain equation needs to be improved before models to predict T_{cv} can be formulated. The prediction of slag viscosity is complicated by the evidence from HT-XRD that the experimental viscosity measurements are being made on a two-phase system of liquid material and solid crystals with crystalline phases forming in the slag melt well above the experimental T_{250} and freezing points of the slag. Viscosity predictions will have to consider the rheological properties of a suspended solid in the slag, as well as the properties of the liquid slag itself.

Calculating the viscosity of liquid-solid slag mixtures depends on the ability of a thermodynamic equilibrium program such as FACT to accurately predict the amount of solid phases present.

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APPENDIX A

EXAMPLE OF OUTPUT FOR ASH TRANSFORMATION MODEL

ENTRAINED FLY ASH
PREDICTED FROM ADVANCED COAL ANALYSIS

AERO. DIAMETER	0.0-1.0	1.0-3.0	3.0-10.0	10.0-30.0	30.0-50.0	UNUSED	Tot.
QUARTZ	0.00	0.00	0.00	0.00	0.00	0.00	0.00
IRON OXIDE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PERICLASE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RUTILE	0.00	0.00	0.00	0.67	0.00	0.00	0.67
ALUMINA	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CALCITE	0.00	0.00	0.10	0.04	0.00	0.00	0.14
DOLOMITE	0.00	0.00	0.04	0.00	0.00	0.00	0.04
ANKERITE	0.00	0.01	1.25	0.50	0.00	0.00	1.76
KAOLINITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MONTMORILLONITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K AL-SILICATE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FE AL-SILICATE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CA AL-SILICATE	0.00	0.00	1.52	6.67	0.00	0.00	8.19
NA AL-SILICATE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ALUMINOSILICATE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MIXED AL-SILICATES	0.00	0.00	0.00	0.08	0.00	0.00	0.08
FE SILICATE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CA SILICATE	0.00	0.00	9.23	12.13	0.00	0.00	21.36
CA ALUMINATE	0.00	0.00	0.10	0.01	0.00	0.00	0.11
PYRITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PYRRHOTITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
OXIDIZED PYRRHOTITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GYPSUM	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BARITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
APATITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CA AL-P	0.00	0.00	0.27	0.46	0.00	0.00	0.72
KCL	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GYPSUM/BARITE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
GYPSUM/AL-SILICATE	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SI-RICH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CA-RICH	0.00	1.05	0.62	0.00	0.00	0.00	1.66
CA-SI RICH	0.00	0.00	0.33	0.44	0.00	0.00	0.76
UNKNOWN	0.00	0.02	17.94	16.34	0.45	0.00	34.75
TOTAL	0.00	1.07	31.39	37.33	0.45	0.00	70.24

NUCLEATED FLY ASH AVERAGE COMPOSITION(OxIDES)

NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
1.60	2.90	12.00	10.90	0.00	0.00	0.00	1.10	54.60	14.70	0.00	2.30

BULK COMPOSITION OF FLYASH AS OXIDES

NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
1.7	6.6	15.5	25.3	0.5	0.0	0.0	0.7	38.1	9.9	0.0	1.6

BULK COMPOSITION OF < 1.0 MICRON ASH

WEIGHT PERCENT			9.52								
NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
1.6	2.9	12.0	10.9	0.0	0.0	0.0	1.1	54.6	14.7	0.0	2.3

BULK COMPOSITION OF 1.0-3.0 MICRON ASH

WEIGHT PERCENT			21.31								
NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
1.8	3.0	11.8	11.1	0.0	0.0	0.0	1.1	55.1	14.0	0.0	2.2

BULK COMPOSITION OF 3.0-10.0 MICRON ASH

WEIGHT PERCENT			31.39								
NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
2.1	10.1	17.7	21.9	0.6	0.0	0.0	0.4	37.2	8.9	0.0	1.1

BULK COMPOSITION OF 10.0-30.0 MICRON ASH

WEIGHT PERCENT			37.33								
NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
1.5	6.6	16.4	40.0	1.0	0.0	0.1	0.6	25.2	7.2	0.0	1.4

BULK COMPOSITION OF 30.0-50.0 MICRON ASH

WEIGHT PERCENT			0.45								
NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
0.3	13.6	38.0	25.7	0.0	0.0	0.0	0.0	12.4	8.7	0.0	1.3

BULK COMPOSITION OF NOT USED MICRON ASH

WEIGHT PERCENT			0.00								
NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

After Size Segregation in Box

0.0-1.0 Micron Ash	9.57
1.0-3.0 Micron Ash	21.41
3.0-10.0 Micron Ash	31.53
> 10.0 Micron Ash	37.50

BULK COMPOSITION OF ENTRAINED ASH

NA2O	MGO	AL2O3	SIO2	P2O5	SO3	CL2O7	K2O	CAO	FE2O3	BAO	TIO2
1.8	6.6	15.4	25.3	0.5	0.0	0.0	0.7	38.2	9.9	0.0	1.6

APPENDIX B

EXAMPLE OF THE TRACE ELEMENT OUTPUT FILE

TRACE ELEMENT COMPOSITION PPM/Size Range

	As	Cd	Cr	Pb	Ni	Se	Hg	%Ash
Vapor	0.0	0.0	0.0	0.0	0.0	11.1	0.7	
1 <	128.1	31.7	341.4	246.0	769.4	122.4	0.0	6.7
1.0-3.0	30.3	7.5	90.0	61.5	183.3	30.6	0.0	3.2
3.0-10.0	3.2	0.6	110.2	13.3	47.8	6.6	0.0	20.9
10.0-30.0	5.7	1.0	240.2	22.1	99.8	10.9	0.0	59.8
30.0-50.0	4.7	0.8	188.8	18.6	79.3	9.2	0.0	9.4
>50	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bulk	14.1	3.2	210.1	36.1	134.4	21.5	0.2	

TRACE ELEMENT COMPOSITION PPM/Total Ash

	As	Cd	Cr	Pb	Ni	Se	Hg
Vapor	0.0	0.0	0.0	0.0	0.0	11.1	0.7
1 <	8.6	2.1	22.8	16.4	51.4	8.2	0.0
1.0-3.0	1.0	0.2	2.9	2.0	6.0	1.0	0.0
3.0-10.0	0.7	0.1	23.0	2.8	10.0	1.4	0.0
10.0-30.0	3.4	0.6	143.6	13.2	59.6	6.5	0.0
30.0-50.0	0.4	0.1	17.8	1.8	7.5	0.9	0.0
>50	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Bulk	14.1	3.2	210.1	36.1	134.4	21.5	0.2

ENTRAINED FLY ASH

PREDICTED FROM ADVANCED COAL ANALYSIS

	As	Cd	Cr	Pb	Ni	Se	Hg	Total
QUARTZ	0.0	0.0	0.3	0.1	0.2	0.0	0.0	0.6
IRON OXIDE	0.1	0.0	47.0	0.4	16.7	0.2	0.0	64.5
PERICLASE	0.0	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	0.0
ALUMINA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CALCITE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
DOLOMITE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ANKERITE	0.0	0.0	0.3	0.0	0.1	0.0	0.0	0.4
KAOLINITE	0.0	0.0	0.4	0.0	0.1	0.0	0.0	0.6
MONTMORILLONITE	0.0	0.0	0.2	0.0	0.1	0.0	0.0	0.2
K AL-SILICATE	0.0	0.0	0.4	0.0	0.1	0.0	0.0	0.6
FE AL-SILICATE	1.3	0.2	44.1	4.9	18.8	2.4	0.0	71.7
CA AL-SILICATE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NA AL-SILICATE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ALUMINOSILICATE	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1
MIXED AL-SILICATES	0.0	0.0	1.7	0.1	0.6	0.1	0.0	2.5
FE SILICATE	0.1	0.0	3.8	0.5	1.7	0.2	0.0	6.4
CA SILICATE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CA ALUMINATE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
PYRITE	0.0	0.0	6.5	0.1	2.2	0.1	0.0	9.0
PYRRHOTITE	0.0	0.0	1.4	0.1	0.5	0.1	0.0	2.2
OXIDIZED PYRRHOTITE	0.0	0.0	2.7	0.1	1.0	0.1	0.0	3.9
GYPSUM	0.0	0.0	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	0.0	0.0
APATITE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CA AL-P	0.0	0.0	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	0.0	0.0
GYPSUM/BARITE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GYPSUM/AL-SILICATE	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SI-RICH	0.2	0.0	2.1	0.9	1.5	0.4	0.0	5.1
CA-RICH	0.0	0.0	0.4	0.1	0.2	0.1	0.0	0.9
CA-SI RICH	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
UNKNOWN	2.6	0.5	82.7	10.1	36.5	5.0	0.0	137.3
TOTAL	4.5	0.8	194.3	17.6	80.4	8.7	0.0	306.4

NUCLEATED FLY ASH AVERAGE COMPOSITION, PPM

As	Cd	Cr	Pb	Ni	Se	Hg
9.5	2.4	25.3	18.2	57.0	9.1	0.0

APPENDIX C

PAPER WITH ADDITIONAL TESTING RESULTS

Predicting Ash Particle Size and Composition Distribution Produced During Pulverized-Coal Combustion

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The size and composition of ash particles produced during pulverized-coal combustion have a major impact on their fate in combustion systems. The size and composition of the ash influence the formation of ash deposits and the performance of particulate control devices. An ash transformation model, Atran, was developed at the Energy & Environmental Research Center (EERC) to predict the size and composition of ash particles and is used in other computer models to predict ash deposition in combustion systems. The inputs to the model include size, composition, and abundance of mineral grains in the coal as determined by computer-controlled scanning electron microscopy; bulk ash composition; ultimate analysis; and abundance of inorganic elements organically associated. Processes such as vaporization/condensation, ash mineral coalescence, partial coalescence, ash shedding, and char fragmentation during char combustion and mineral fragmentation have been incorporated into the model and all play an important role in the size and composition of the final fly ash. The size and composition distribution of the entrained ash produced from lignite, subbituminous, and bituminous coals in full-, pilot-, and laboratory-scale combustion systems have been compared to the predictions made with Atran. The entrained ash was collected and aerodynamically classified. The sized fractions were analyzed to determine chemical compositions. The particle-size and composition distributions for 6000 particles for each coal were calculated using Atran and then binned by size and composition for comparison with ash collected. The model predictions and actual measurements compared very favorably.

Introduction

Inorganic coal components undergo complex chemical and physical transformations during combustion to produce vapors, liquids, and solids in the combustion system. The partitioning of the inorganic components during combustion to form vapors, liquids, and solids depends upon the association and chemical characteristics of the inorganic components, the physical characteristics of the coal particles, the physical characteristics of the coal minerals, and the combustion conditions. The physical transformation of inorganic constituents depends on the inorganic composition of the coal and combustion conditions. The inorganic components can consist of organically associated cations, mineral grains that are included in coal particles, and excluded mineral grains. There is a wide range of combinations of mineral–mineral, mineral–coal, mineral–cation–coal, and mineral–mineral–cation–coal associations in coal. These associations are unique to each coal sample. The physical transformations involved in fly ash formation include 1) coalescence of individual mineral grains within a char particle, 2) shedding of the ash particles from the surface of the chars, 3) incomplete coalescence due to disintegration of the char, 4) convective transport of ash from the char surface during devolatilization, 5) fragmentation of the inorganic mineral particles, 6) formation of cenospheres, and 7) vaporization and subsequent condensation of the inorganic components upon gas cooling. Combustion conditions and temperature profiles in the boiler will influence the physical transformation mechanisms involved in ash formation. As a result of these interactions, the ash size distribution is generally bimodal, with the submicron component largely a result of the condensation of the flame-volatilized inorganic component and the supermicron fraction being from the mineral grains combined with cations (Loehden and others, 1989; Zygarricke and others, 1990). Numerous studies have been conducted to quantify the physical transformation mechanisms (Benson and others, 1993b).

The ash transformation model (Atran) was developed to predict the size and composition of ash particles produced during coal combustion. The code has been described in detail by Hurley and coworkers (1992). Atran is a key component in other models developed at the Energy & Environmental Research Center (EERC), including TraceTran and Fuel Quality Advisor (FQA). TraceTran was developed based on Atran to predict particle-size and composition distributions (PSCD) of major, minor, and trace elements of interest in combustion and gasification systems (Erickson and others, 1998). The Tracetrans model was designed for a gasification system and will predict trace elements. FQA is used to predict high- and

low-temperature convective pass fouling behavior. The code provides deposit growth rates, deposit removability, and effects on heat transfer (Benson and others, 1993a).

This paper describes tests conducted with the Atran code to optimize key input information such as combustion parameters that will influence fragmentation and coalescence of minerals and heterogeneous and homogeneous interaction of organically associated cations. A Powder River Basin (PRB) subbituminous coal from the Rochelle Mine was combusted in the conversion and environmental process simulator (CEPS), and the ash produced was collected and aerodynamically sized, with each size fraction being analyzed for major and minor element composition. The information was then compared to the predicted results from the ash transformation model.

Experimental Methods

The Atran model requires computer-controlled scanning electron microscopy (CCSEM), x-ray fluorescence (XRF), and ultimate analysis of the fuel and boiler design and operating parameters in order to predict the size and composition distribution of the ash. In this study, Rochelle coal was analyzed to determine the size, composition, abundance, and association of mineral grains using CCSEM (Zygarlicke and Steadman, 1990); bulk ash composition by XRF; and C, H, N, O, and S by ultimate analysis. The CCSEM analysis is also combined with a locked/liberated particle analysis to determine if the individual mineral grains are located within a coal matrix or are free mineral grains.

The ash was produced in the CEPS combustion system when firing Rochelle coal. The CEPS is pilot-scale combustor designed to nominally top-fire pulverized coal, with a heat input of 40,000 Btu/hr. The CEPS was operated at a coal feed rate of 1.4 kg/hour, 25% excess air, a 1500°C initial combustion temperature, and an 1100°C convective pass inlet temperature. A portion of the particulate was removed before the convective pass section of the CEPS. The fly ash was sampled using a source assessment sampling system (SASS) train. The SASS train is equipped with three cyclones and a backup filter used to aerodynamically classify the ash into the following size fractions < 1, 1–3, 3–10, and 10–50 micrometers.

Coal composition, boiler design, and operating conditions were used as input parameters into the Atran model to determine the size partitioning of the inorganic species during fly ash formation for Rochelle coal. With these inputs, the Atran model begins by calculating a mass balance on the inorganic composition by comparing the CCSEM mineral composition and bulk ash composition data. The balance provides the compositions of locked minerals (in the coal matrix) and liberated minerals (outside the coal matrix) and type and abundance of organically associated constituents. Once the mass balance is complete, the distribution of the cations for homogeneous and heterogeneous condensation and interaction and the degree of fragmentation and coalescence of mineral grains are defined based on boiler design and operating conditions. The boiler design and operating conditions specifically define a file called "homohet" that is used to determine the percentage of the major elements (Na, Mg, Al, Si, P, K, Ca, Ti, and Fe), which is distributed between homogeneous and heterogeneous along the percentage of the homogeneously nucleated particles that are submicron. The organically associated cations go through a vaporization step and then are split between heterogeneous condensation and homogeneous condensation. The heterogeneous condensation step distributes the particles into the supermicron fly ash size bins along with the homogeneous condensation agglomerations. The remaining homogeneous condensation particles are distributed into the submicron fly ash size bins. Boiler design and operational parameters are linked to fragmentation and coalescence factors for mineral grains, including pyrite, iron carbonate, pyrrhotite, gypsum, barite, Ca–Al–P, kaolinite, dolomite, and quartz. A fragmentation is then applied to both the locked and liberated particles. Coalescence and shedding are applied to the locked particles before the heterogeneous condensation stage. The liberated particles go directly into the heterogeneous condensation step. The ash is then partitioned and run through a mass balance calculation to yield a predicted PSCD. The homogeneous/heterogeneous and fragmentation/coalescence values need to be optimized for specific boiler designs and operating conditions.

Results and Discussion

The homogeneous/heterogeneous and fragmentation/coalescence values were optimized and used in Atran to predict the PSCD of the ash produced from Rochelle coal. The predicted results are compared with the measured composition of the aerodynamically classified particles produced upon combustion of the Rochelle coal as shown in Figure 1. Atran also predicts the weight percent of ash in the various size fractions and is shown in Figure 2. In general, the SiO₂ levels in the various size fractions compare well with the predicted values for all size fractions. The predicted CaO levels compare well with the predicted values for the <10-micrometer size fractions. The CaO content in the >10-micrometer-sized ash particles was found to be higher than the predicted. The higher level of CaO may be due to the loss of larger particles in the CEPS

Figure 1. Comparison of the composition of the predicted and measured ash compositions.

Figure 2. Comparison of the predicted mass in the various size fractions.

after the gas stream passes through the convective pass or may be due to underpredicting the interaction of the organically associated calcium with the coalescing mineral during combustion. Differences were also noted between the predicted and measured Al_2O_3 contents. The differences may be due to the fact that some of the aluminum in PRB coals is associated as a mineral that is composed of high levels of calcium, aluminum, and phosphorus similar in composition to crandalite. The exact transformations of crandalite have not yet been established. The Fe_2O_3 content compares well with the particles >3 micrometers; however, for the smaller particles, Atran is overestimating the levels of Fe_2O_3 .

The predicted size distribution shows some differences for the two larger-size fractions of ash and good agreement for the smaller sizes. The primary reason for the differences is likely due to the loss of some of the larger particles in the CEPS as the particles enter the convective pass of the furnace.

Conclusions

The homogeneous/heterogeneous and fragmentation/coalescence values must be optimized for various firing systems and firing conditions. The predicted results compared with the measured composition of the aerodynamically classified particles produced upon combustion of the Rochelle coal show generally good agreement. The SiO_2 levels in the various size fractions compare well with the predicted values for all size fractions. The predicted CaO levels compare well with the predicted values for the <10-micrometer-size fractions. The CaO content in the >10-micrometer-sized ash particles was found to be higher than the predicted. Differences were also noted between the predicted and measured Al_2O_3 contents. The Fe_2O_3 content compares well with the particles >3 micrometers; however, for the smaller particles, Atran is overestimating the levels of Fe_2O_3 . The predicted size distribution shows some differences for the two larger-size fractions of ash and good agreement for the smaller sizes. The primary reason for the differences is likely due to the loss of some of the larger particles in the CEPS as the particles enter the convective pass of the furnace.

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