TASK 3.1 – LOW-TEMPERATURE ASH SINTERING AND STRENGTH DEVELOPMENT

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TASK 3.1 – LOW-TEMPERATURE ASH SINTERING AND STRENGTH DEVELOPMENT

INTRODUCTION

The loss of efficiency due to ash deposition on heat exchange surfaces is a constantly occurring problem for the fossil fuel and biomass-fired power industry. Although significant progress has been made in the understanding and prediction of deposit formation, the estimation of the ease of removability of deposits by sootblowing has lagged. The current trend toward burning coal–biomass blends has the potential for producing even more problematic deposits because of the high alkali content of the biomass component of the ash.

The understanding of ash agglomeration, deposit growth, and strength development in combustion systems requires basic knowledge of mass transfer phenomena at liquid–solid interfaces, dynamic and kinematic viscosities, and interfacial surface tensions. Measurements in the viscosity range of interest for ash deposition, 10^6 – 10^{10} Pa s (10^7 – 10^{11} poise), cannot be performed by conventional bulk viscosity methods such as rotating-bob viscometry or penetrometry. Further, experimental verification of models used to predict ash viscosity, such as those based on the Urbain equation (1, 2) are generally performed at much lower viscosities, in the 10^2 Pa s (10^3 poise) range.

Despite the significance of viscosity on ash deposit formation in combustion systems, very little experimental work on ash particle interaction has been performed in the high-end 10^5 – 10^9 poise regime. The pioneering work of Frenkel (3) provided a sintering model of the coalescence of two spheres relating viscosity and surface tension to the measurable quantities of particle radius and the rate of neck growth with time. Limited experimental determinations of sintering rates of glassy particles have been performed by Kuczynski (4) and of coal ash particles by Raask (5) employing the Frenkel model.

Previous work used a heated-stage microscope (HSM) for analyzing particle-to-particle sintering rates using uniform spheres produced from a commercial soda-lime glass and from an Illinois No. 6 slag. The technique is based on measuring the rate of growth of the neck formed between two touching particles as they sinter. The results indicated a linear increase in neck diameter with time rather than an increase proportional to the square of the neck diameter as predicted by the Frenkel equation. Viscosities calculated from these previous results compared fairly well to the predicted value based on composition and temperature calculated from a modified version of the Urbain viscosity model.

OBJECTIVES

The objective of the project is to develop fundamental sintering–viscosity relationships for coal-type ash at relatively low temperatures, with the end result being a simplified sootblowing index for power systems. This involves correlating several important factors which control the

ease of deposit removal, including deposit strength, deposit porosity, chemical composition, and temperature.

STATEMENT OF WORK

Testing was performed on ashes derived from three coals and two biomass materials along with a standard soda-lime glass. The coals were selected because detailed analyses as well as ash samples were already available. Sintering characteristics of the ashes were to be determined by observation using an HSM and video recording system, with a stainless steel microscope stage chamber constructed to allow the use of corrosive gas atmospheres. The measurements would allow calculation of the viscosity of liquid phases as the sintering progressed, using the Frenkel and other sintering models.

The sintering behavior and viscosity would be correlated with ash mineralogy and chemistry and information on bench-scale deposit strength and porosity to develop an initial relationship to predict deposit removability.

ACCOMPLISHMENTS

Selection of Coals and Biomass Materials

Six materials were used for HSM sintering experiments: a glass of certified composition (Standard Reference Material 710a soda-lime-silica glass), a slag produced from the combustion of an Illinois No. 6 bituminous coal, ashes produced from Rochelle and North Antelope subbituminous coals, and ashes produced from wheat straw and alfalfa stem biomass material. Properties of the model glass, such as viscosity and surface tension, were available in the literature. The majority of the coals and biomass as well as their ashes had been previously characterized by the EERC.

The soda-lime glass and the Illinois No. 6 coal slag had been previously prepared for HSM experiments by a process of homogenizing by repeated crushing and remelting, sizing, and melting into spheres by passing through a drop-tube furnace (DTF) at 1300 °C and residence time of 1.2 seconds. The DTF products were examined by scanning electron microscopy (SEM) to verify that good sphericity had been obtained. The glass and coal slag spheres were sized for use by being sonic-sieved to a size range of 20–38 µm.

The Rochelle and North Antelope ashes were formed into spherical particles by passing through the DTF under conditions similar to those used for the glass and Illinois No. 6 slag and sonic-sieved to a size range of 20–38 µm. Unlike the glass and slag, these ashes were not melted to homogenize them prior to producing the spheres, as it was desired to observe the sintering behavior of particles with a range of compositions similar to that occurring in an actual ash deposit.

Ashes derived from wheat straw and from alfalfa stems were prepared by ashing samples of these biomass materials in a muffle furnace under conditions similar to those used for ASTM (American Society for Testing and Materials) ashing. Because of the high potassium and chlorine content of these fuels, no attempt was made to prepare spherical particles in the DTF, as this was expected to volatilize a significant portion of the ash material and alter the ash composition.

Apparatus and Sintering Test Procedures

The sintering measurements were performed using a Leitz HSM in the configuration shown in Figure 1. The apparatus comprised a Leitz Metallux II optical microscope with a water-cooled heating stage rated to 1750 °C; a tantalum (Ta) heating strip; a black-and-white video camera and videotape recorder for recording the progress of sintering; a PC with a single A/D channel for logging temperatures; and a video mixer to overlay computer-displayed time, temperature, and other test information on the video record. A 0.4-mm Type S thermocouple attached to the heating strip with high-temperature ceramic cement provided temperature monitoring and control. A temperature controller was incorporated into the HSM electrical power supply. Problems in maintaining a constant temperature with the controller led to maintaining temperature control by manually adjusting two variable autotransformers connected in series, allowing a near constant (± 5 °C) strip temperature to be maintained.

Particles were transported to the heating strip within the HSM on the tip of a needle. The needle was tapped lightly on the surface of the heating strip to deposit the particles. The strip was searched under microscope to identify a pair (or pairs) of particles of the same approximate size and which appeared to be in contact. The temperature then ramped up at approximately

Figure 1. Sintering apparatus configuration.

150 °C/min until the selected temperature was reached and held constant thereafter. The HSM heated stage was purged with a slow flow (10 cm³/min) of argon gas. Temperature and video logging and video were initiated when the run temperature was attained. The videotape recorder provided a continuous record of the sintering behavior of the particles under observation, with the video mixer superimposing time and temperature data on the video image. Upon completion of a sintering test, the video tape was reviewed and particle radius and neck growth measurements obtained for the selected pairs of sintered particles as a function of time. Measurements were taken from the images on the video monitor using the video recorder freeze-frame capability. To provide a size calibration reference, a standard grid on a microscope calibration slide as well as standard glass beads obtained from Duke Scientific Company, 31.9 ± 2.2 µm in size, were imaged and recorded prior to sintering tests. Calibration of the HSM strip temperature was done using standards of known melting points: lead wire (327 °C), sodium sulfate (884 °C), and copper wire (1083 °C), and recorded (thermocouple) temperatures were corrected using a regression equation of indicated versus actual melting points. Calibrations were checked with sodium sulfate when the heating strip or thermocouple were changed. Temperatures reported for the particle sintering results are corrected temperatures using this calibration.

The sintering temperatures of the materials were identified using the HSM. Two particles of similar size were viewed during heating to observe when rapid sintering began and when melting of the spheres occurred. Three temperatures were then chosen (nominally 20 –50 °C less than the onset of the rapid sintering temperature) to provide measurably long sintering durations for the sintering tests.

Sample Analysis

Bulk chemistry of the soda-lime glass, the Illinois coal slag spheres, and the subbituminous coals and the biomass ashes were determined using x-ray fluorescence (XRF) analysis. The biomass samples were examined for inorganic materials present using computer-controlled scanning electron microscopy (CCSEM). Chemical fractionation (CHF) analysis was performed on the alfalfa stem material, along with proximate and ultimate analyses on both the wheat straw and alfalfa stem materials. CCSEM, CHF, and proximate-ultimate analysis of the coals were obtained from previous existing analyses.

RESULTS

Sample Analysis

The proximate-ultimate analyses of the fuels as well as the bulk ash chemistry of the fuels are given in Tables 1 and 2, respectively. The Illinois No. 6 slag was formed in the Central Illinois Public Service Coffeen Plant cyclone boiler firing a Illinois No. 6 bituminous coal. The higher than usual calcium content is due to limestone blended with the coal prior to combustion to reduce the slag viscosity. The Rochelle and North Antelope ashes were collected as baghouse ash produced from sub-pilot-scale combustion testing in the combustion and environmental

TABLE 1

Proximate and Ultimate Analyses of the Fuels

As-Received, wt%					
Fuel	Illinois No. 6	Rochelle	North Antelope	Wheat Straw	Alfalfa Stems
Proximate Analysis					
Moisture	8.40	22.90	26.60	9.60	7.80
Volatile Matter	36.24	36.43	34.37	74.40	82.92
Fixed Carbon	44.61	36.18	34.88	8.38	5.35
Ash	10.75	4.49	4.14	7.62	3.93
Ultimate Analysis					
Hydrogen	5.48	6.32	6.85	5.91	6.11
Carbon	64.30	54.67	51.81	38.29	41.83
Nitrogen	1.03	0.66	0.64	0.76	1.64
Sulfur	3.42	0.30	0.26	0.23	0.12
Oxygen	15.02	33.50	36.30	47.18	46.37
Ash	10.75	4.55	4.14	7.62	3.93
Heating Value, Btu/lb	11,745	9175	9355	6462	7112

TABLE 2

Bulk Ash Chemistry of the Fuels

wt%						
Material	Glass Beads	Illinois No. 6	Rochelle	North Antelope	Wheat Straw	Alfalfa Stems
SiO ₂	71.21	53.10	27.13	29.13	20.80	30.00
Al ₂ O ₃	0.00	20.30	16.04	15.95	1.60	0.50
Fe ₂ O ₃	0.67	14.20	6.51	6.23	1.20	0.70
TiO ₂	9.83	0.90	1.31	1.11	0.20	0.10
P ₂ O ₅	0.15	0.20	0.81	0.99	11.20	8.70
CaO	0.23	3.40	23.15	25.35	25.90	25.10
MgO	2.78	1.60	6.86	9.85	5.40	4.30
Na ₂ O	14.75	1.30	1.51	0.99	1.10	1.50
K ₂ O	0.00	2.10	0.25	0.32	31.40	27.90
SO ₃	0.32	2.90	16.44	10.07	1.30	1.20

process simulator (CEPS) at the EERC. The wheat straw and alfalfa were purchased in bale form from local farmers. The alfalfa was subjected to repeated manual brushing across a large mesh screen to separate the leaves from stems and obtain a sample of relatively pure stem material.

Sintering Rate Measurements

Particle radius and neck growth measurements were obtained by reviewing the videotaped sintering runs. Neck growth measurements were more difficult to obtain for the Illinois No. 6 slag, the North Antelope ash, as the particle coloration was similar to that of the heated stage background. The wheat straw ash had extremely poor contrast, with measurements made only before heating and after cooling of the sample subsequent to the sintering test. No sintering measurements could be obtained for the alfalfa stem ash, because no sintering was observed up to the limiting temperature of 1180 °C for the heating stage used, although a small degree of sublimation was seen to occur. For the other materials, the particle radius and neck growth measurements were used to calculate the degree of sintering (x/r), where x is the radius of the sintering neck and r is the arithmetic average radius of the sintering particles.

Figure 2 shows values of x/r plotted against time (s) for each of the materials at three temperatures below the sintering point. The replicate plots at each temperature represent different pairs of sintered particles and give an indication of the repeatability of the data. Previous testing had shown the need to obtain measurements over the entire range of neck growth from onset to complete fusing of the particles under observation.

Viscosity Calculations Based on the HSM Measurements

The particle radius and neck growth measurement data were utilized to calculate the dynamic viscosity using four analytical models for sintering: Frenkel (5), Frenkel–Eshelby (6, 7), Hopper (8, 9), and a Modified Frenkel model (10). A fifth model, adapted from Washburn’s model of capillary flow in porous media (11), was also compared with the analytical models, as it offered a potential simplification of the HSM measurement process.

Frenkel’s model, given in Eq. 1, describes the rate of coalescence occurring by Newtonian viscous flow under the action of surface tension for two identical spheres:

$$x/r = [1.5 (\gamma t)/(\eta r)]^{1/2} \quad [\text{Eq. 1}]$$

where η = viscosity (Pa · s)
 x = radius (m) of neck between two spherical particles
 t = time (sec)
 r = particle radius (m) at time t
 γ = surface tension (N/m)

(a)

Figure 2. Values of x/r versus time: a) soda-lime glass, b) Illinois No. 6 slag, c) Rochelle ash, and d) North Antelope ash.

(b)

(c)

(d)

Frenkel's model was corrected by Eshelby to satisfy the continuity equation for an incompressible fluid. The corrected model, referred to here as the Frenkel–Eshelby model (Eq. 2), and the Frenkel model are both limited to Newtonian flow and only in the early stages of sintering when the particle diameters remain relatively constant, i.e., $x/r < 0.3$.

$$x/r = [(\gamma t)/(\eta r)]^{1/2} \quad [\text{Eq. 2}]$$

Hopper's model for sintering is based on the exact analytical solution of the Navier–Stokes equation for two-dimensional viscous flow driven by capillary forces acting on the free surface. Hopper's analysis was applied to two long cylinders having an inverse ellipse as their cross section.

The Modified Frenkel model, as developed by Pokluda, Bellehumeur, and Vlachopoulos, is based on an approach similar to that used by Frenkel and Eshelby in their model derivations. In contrast to the Frenkel and Frenkel–Eshelby models, the Modified Frenkel model is applicable to all stages of spherical particle sintering. Further, the Modified Frenkel model considers the change in particle radius as sintering progresses.

Obtaining analytical solutions of the Hopper and Modified Frenkel models is not a trivial task. Fortunately, values of dimensionless time $[(\gamma t)/(\eta r_f)]$ and the corresponding degree of sintering (x/r_f) have been computed by Hopper (8) and are given in Table A-1, Appendix A. Similarly, values of $[(\gamma t)/(\eta r_o)]$ and x/r have been computed by Pokluda, Bellehumeur, and Vlachopoulos (10) and are given in Table A-2, Appendix A. The variable r_f is the final particle radius for the Hopper model, and r_o is the initial particle radius for the Modified Frenkel model.

For this study, a best-fit curve was generated from the tabulated values (dimensionless time, τ , and degree of sintering, X) for both the Hopper and Modified Frenkel models. The general equations for the best-fit curves for the Hopper and Modified Frenkel models are shown in Equations 3 and 4, respectively:

$$\tau = [(a + cX + eX^2)/(1 + bX + dX^2 + fX^3)] \quad [\text{Eq. 3}]$$

$$\tau = [(a + cX^2 + eX^4)/(1 + bX^2 + dX^4 + fX^6)] \quad [\text{Eq. 4}]$$

The independent variable X is (x/r_f) for the Hopper model and (x/r) for the Modified Frenkel model. Similarly, the dependent variable τ is $[(\gamma t)/(\eta r_f)]$ for the Hopper model and $[(\gamma t)/(\eta r_o)]$ for the Modified Frenkel model. For the Hopper model, r_f is $r_o(2)^{1/2}$. Coefficients a , b , c , d , e , and f for both models are presented in Table 3.

The model adopted from Washburn's model of capillary flow is strictly correct for flow in a single cylindrical tube and is given in by Equation 5:

TABLE 3

Coefficients for the Hopper and Modified Frenkel Equations						
Model	Coefficient					
	a	b	c	d	e	f
Hopper	0.0136	1.3067	0.82496	0.1083	0.7982	0.4169
Modified Frenkel	0.00043	1.0780	1.0049	0.3021	0.5881	0.0103

$$L^2 = (\gamma) D t / 4 (\nu) \quad [\text{Eq. 5}]$$

where L is the penetration distance into the porous material, (γ) and (ν) are the surface tension and viscosity, respectively, D is the pore diameter, and t is the time required for penetration distance L . For the purposes of obtaining a viscosity from the sintering test data, the pore diameter D was taken as the average initial diameter of the two sintering particles, and L the length of the two particles when fused into a single oval particle with no discernible intervening neck at time t . Preliminary calculations gave surprisingly close agreement with viscosities calculated from the other four equations. It was found that a value of L being the single particle length divided by approximately the value of π gave viscosity values very close to those of the other equations for the glass beads, although this empirical correlation is not based on a rigorous derivation. The advantage of this model is that only the initial particle diameters, the final length of the fused particle, and the time taken to achieve this need be experimentally measured.

Dynamic viscosity values were calculated from each of the first four models for each x/r (and corresponding t) value. The Frenkel and Frenkel–Eshelby models, Eqs. 1 and 2, respectively, were rearranged to solve for the unknown variable, η . When applying the Hopper and Modified Frenkel models, Equations 3 and 4 were each used to compute dimensionless time values (τ) for each corresponding x/r value. The dynamic viscosity was then calculated from Equation 6.

$$\eta = (\gamma t) / (\tau r) \quad [\text{Eq. 6}]$$

where r is r_f from the Hopper model or r_o from the Modified Frenkel model. The surface tension (γ) value for the soda-lime glass was taken as 0.304 N/m. As an approximation, the same value was used as the surface tension for the ash materials. A single viscosity was also predicted for each test using the Washburn model.

The dynamic viscosity values computed from the models are presented in Table 4 for the soda-lime glass, the Illinois No. 6 slag, and for the ashes. The value presented for each pair of sintered particles for the first four models is an arithmetic average of the dynamic viscosities

TABLE 4

Viscosity Values Calculated by the Models

Viscosity Values Calculated by the Model							Modified		
	Particle Average Diameter, μm	Number of Measurements		Frenkel Model Viscosity Log_{10} Poise	Frenkel–Eshelby Model Viscosity Log_{10} Poise	Hopper Model Viscosity Log_{10} Poise	Frenkel Model Viscosity Log_{10} Poise	Washburn Model Viscosity Log_{10} Poise	Bulk Composition Viscosity Log_{10} Poise
Soda-Lime Glass									
625	33.0	16	Average	8.20	8.02	7.58	7.80	7.86	8.03
			Standard Deviation	0.15	0.15	0.22	0.31		
625	34.0	12	Average	8.22	8.04	7.65	7.93	7.72	8.03
			Standard Deviation	0.08	0.08	0.11	0.09		
641	34.5	14	Average	7.93	7.76	7.38	7.54	7.81	7.79
			Standard Deviation	0.11	0.11	0.16	0.19		
641	33.5	10	Average	7.73	7.55	7.15	7.26	7.73	7.79
			Standard Deviation	0.06	0.06	0.14	0.13		
665	30.0	5	Average	7.26	7.08	6.65	6.61	7.24	7.46
			Standard Deviation	0.04	0.04	0.24	0.30		
665	32.0	5	Average	7.29	7.11	6.75	6.71	7.22	7.46
			Standard Deviation	0.04	0.04	0.11	0.25		
Illinois No. 6 Slag									
841	15.0	9	Average	8.23	8.06	7.69	7.75	8.63	6.61
			Standard Deviation	0.13	0.13	0.09	0.30		
841	20.0	8	Average	8.20	8.02	7.60	7.62	8.51	6.61
			Standard Deviation	0.11	0.11	0.10	0.29		
865	26.0	10	Average	7.96	7.79	7.38	7.60	8.39	6.36
			Standard Deviation	0.11	0.11	0.06	0.19		
865	26.0	8	Average	8.04	7.86	7.47	7.76	8.39	6.36
			Standard Deviation	0.08	0.08	0.09	0.12		
889	22.5	3	Average	7.86	7.68	7.31	7.56	8.46	6.11
			Standard Deviation	0.08	0.08	0.05	0.16		
889	22.5	7	Average	7.84	7.66	7.33	7.48	8.46	6.11
			Standard Deviation	0.11	0.11	0.13	0.07		
Rochelle Ash									
657	40.0	42	Average	8.32	8.15	7.80	7.89	8.21	5.04
			Standard Deviation	NA	NA	NA	NA	NA	NA
673	42.5	14	Average	7.67	7.49	7.12	7.00	7.72	4.88
			Standard Deviation	0.09	0.09	0.03	0.26		

Continued . . .

TABLE 4 (continued)

Viscosity Values Calculated by the Models

Viscosity Values Calculated by the Model							Modified		
	Particle			Frenkel	Frenkel–Eshelby	Hopper	Frenkel	Washburn	Bulk
	Average	Number of		Model	Model	Model	Model	Model	Composition
Temperature, °C	Diameter, μm	Measurements		Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity
				Log ₁₀ Poise	Log ₁₀ Poise	Log ₁₀ Poise	Log ₁₀ Poise	Log ₁₀ Poise	Log ₁₀ Poise
673	37.0	11	Average	7.77	7.60	7.23	7.32	7.69	4.88
			Standard Deviation	0.12	0.12	0.07	0.21		
689	42.5	3	Average	7.11	6.94	6.59	6.45	7.15	4.73
			Standard Deviation	0.02	0.02	0.09	0.27		
689	41.5	7	Average	7.40	7.22	6.89	6.84	7.46	4.73
			Standard Deviation	0.15	0.15	0.13	0.08		
North Antelope Ash									
993	32.5	40	Average	8.58	8.40	8.03	8.20	NA	2.79
			Standard Deviation	0.07	0.07	0.09	0.17		
993	29.0	36	Average	8.28	8.11	7.76	7.58	NA	2.79
			Standard Deviation	0.14	0.14	0.13	0.26		
1009	28.0	13	Average	7.81	7.63	7.25	7.10	NA	2.70
			Standard Deviation	0.06	0.06	0.07	0.29		
1009	27.0	15	Average	8.23	8.05	7.67	7.78	NA	2.70
			Standard Deviation	0.14	0.14	0.09	0.32		
1033	39.0	4	Average	7.33	7.15	6.80	6.59	8.25	2.57
			Standard Deviation	0.11	0.11	0.11	0.44		
1033	32.5	7	Average	7.69	7.52	7.20	7.21	8.30	2.57
			Standard Deviation	0.08	0.08	0.10	0.37		
Wheat Straw Ash									
508	78.5	1	Average	NA	NA	NA	NA	7.63	4.74
			Standard Deviation	NA	NA	NA	NA		
508	52.8	1	Average	NA	NA	NA	NA	7.80	4.74
			Standard Deviation	NA	NA	NA	NA		
537	64.5	1	Average	NA	NA	NA	NA	7.19	4.43
			Standard Deviation	NA	NA	NA	NA		
537	58.5	1	Average	NA	NA	NA	NA	7.36	4.43
			Standard Deviation	NA	NA	NA	NA		
564	43.8	1	Average	NA	NA	NA	NA	7.10	4.17
			Standard Deviation	NA	NA	NA	NA		
564	64.8	1	Average	NA	NA	NA	NA	7.02	4.17

Standard Deviation	NA	NA	NA	NA
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calculated at each measured x/r (and t). Owing to the small number of observations for each pair of sintered particles, no data points were excluded from the averaging.

Viscosities were also estimated for the soda-lime glass, the Illinois No. 6 slag, and the ashes from their bulk chemistry using a modified version of the Urbain equation with parameters taken from the literature (2). These predicted viscosity values are also shown in Table 4.

An equilibrium thermodynamic modeling program, FACT (12) was used to estimate the percentages of silicate- and iron-based liquid phases of the test materials as a function of temperature, based on bulk chemistry and the ultimate analyses of the fuels. The ultimate analysis of the soda-lime glass was taken to be that of the Rochelle coal. From the composition of the liquid phases predicted at each temperature, viscosities were calculated using the modified Urbain equation. Plots of the predicted percentage of liquid phases and of liquid-phase viscosity for the materials as a function of temperature are shown in Figures 3 and 4. The wheat straw ash is not shown, as the FACT calculations did not converge for the great majority of the calculations for this material.

CONCLUSIONS AND FUTURE PLANS

Experimental Determination of Viscosity Using the HSM

Determination of viscosity based on observations of sintering using the HSM has proved to be a viable experimental method in the high-viscosity regime encountered in the formation of ash

Figure 3. Percentage of liquid phases predicted by FACT.

Figure 4. Predicted viscosities for liquid-phase material.

deposits. It should be noted that the technique appears to always give viscosity values in the 10^6 – 10^8 poise range, as this is the viscosity range which gives conveniently measurable sintering times of 20–1000 s. This corresponds to viscosity measurements being made in a quite narrow temperature range, usually within approximately 50 °C below the point where rapid sintering occurs. The technique is quite labor-intensive, with the difficulty of obtaining data on a representative number of particles. The low contrast of some ashes relative to the heating stage can also present difficulties in sizing particles and determining neck growth during sintering. The Washburn model appears to provide viscosity values comparable to the other models and, if further validated, may provide a more rapid and simpler method of providing the experimental sintering data.

Determination of Particle Viscosity

Viscosities predicted by the Frenkel, Frenkel–Eshelby, Hopper, and Modified Frenkel models differ by less than 10% for the materials tested. Table 5 gives a condensed summary of the viscosity results, and the results are shown graphically for the Rochelle ash in Figure 5. The wheat straw ash, because of the difficulty in performing sintering measurements, has viscosities calculated only using the Washburn model.

The Frenkel and Frenkel–Eshelby models consistently give somewhat higher viscosities than do the Hopper and Modified Frenkel models. The adaptation of the Washburn model gives viscosities generally higher than those of the other models for the Illinois No. 6 slag and the Rochelle ash, but is quite close to the Frenkel and Frenkel–Eshelby model values for the soda-

TABLE 5

Summary of the Viscosity Results

	Temperature, °C	Particle Average Diameter, μm	Frenkel Model	Frenkel-Eshelby Model	Hopper Model	Modified Frenkel Model	Washburn Model	Bulk Composition
			Viscosity Log_{10} Poise	Viscosity Log_{10} Poise	Viscosity Log_{10} Poise	Viscosity Log_{10} Poise	Viscosity Log_{10} Poise	Viscosity Log_{10} Poise
Soda Glass Beads	625	33.50	8.21	8.03	7.62	7.87	7.79	8.03
	641	34.00	7.83	7.66	7.26	7.40	7.77	7.79
	665	31.00	7.27	7.10	6.70	6.66	7.23	7.46
Illinois No. 6 Slag	841	17.50	8.22	8.04	7.64	7.69	8.57	6.61
	865	26.00	8.00	7.82	7.42	7.68	8.39	6.36
	889	22.50	7.85	7.67	7.32	7.52	8.46	6.11
Rochelle Ash	657	40.00	8.32	8.15	7.80	7.89	8.21	5.04
	673	39.75	7.72	7.54	7.18	7.16	7.71	4.88
	689	42.00	7.26	7.08	6.74	6.65	7.31	4.73
North Antelope Ash	993	30.75	8.43	8.26	7.90	7.89	NA	2.79
	1009	27.50	8.02	7.84	7.46	7.44	NA	2.70
	1033	71.50	7.51	7.34	7.00	6.90	8.28	2.57
Wheat Straw Ash	508	65.63	NA	NA	NA	NA	7.72	4.74
	537	61.50	NA	NA	NA	NA	7.28	4.43
	564	54.25	NA	NA	NA	NA	7.06	4.17

Figure 5. Calculated viscosities for Rochelle ash.

lime glass. In all cases, the viscosities calculated from the models are within an order of magnitude of each other and predict similar viscosity values.

Comparison of the Viscosity Models with Calculated Viscosity

Predictions of viscosities for the soda-lime glass, using the modified Urbain equation, were of the same order of magnitude as predictions generated by the sintering models and nearly the same as the values given by the Frenkel and Frenkel–Eshelby models. However, the Urbain viscosity predictions are approximately 1.5 orders of magnitude lower than the model predictions for the Illinois No. 6 slag and 3 orders of magnitude lower for the Rochelle ash. It is apparent that the Urbain equation predictions significantly underestimate particle viscosity in this low-temperature high-viscosity regime for actual ash materials. This may be expected, as the modified Urbain equation was developed using correlations of chemical composition with viscosity measurements made in the traditional manner at much higher temperatures.

Predictions of the amount and composition of silicate- and iron-based liquid phases for the materials were also performed using FACT equilibrium thermodynamic modeling. The viscosity as a function of temperature was then calculated using the modified Urbain equation from the predicted liquid-phase composition at each calculation temperature. The FACT calculations predict that no liquid phases should exist until up to 100 –300 °C above the temperature at which sintering was experimentally observed to be occurring. In the range where liquid phases were predicted, the liquid-phase viscosities may be either higher or lower than those predicted from the bulk composition.

Figure 6. Experimental and predicted viscosities for Illinois No. 6 ash.

For the Illinois No. 6 coal, Figure 6 shows the experimental viscosities obtained from the sintering measurements (using the Frenkel model) and viscosities obtained from rotating-bob viscometer measurements compared to predicted viscosity using the Urbain equation based on bulk composition and on the composition of liquid phases predicted by FACT. It is seen that the viscosity based on bulk composition is close but somewhat higher than the viscometer measurements, but predicts much lower viscosity at the lower temperatures of the sintering measurements. For this coal, viscosity based on the FACT liquid phases are comparable to the sintering measurements, but predict a much higher viscosity than the viscometer measurements. The fluctuations in the FACT viscosities are due to abrupt changes in the liquid composition as specific solid phases become thermodynamically favored over a narrow temperature range.

These results show that both the FACT thermodynamic model and the modified Urbain equation must be used with caution in the low-temperature region where slow deposit sintering is occurring. The FACT predictions tend to overestimate the temperature at which sintering will occur, thus underpredicting the potential for deposit formation and sintering, while the Urbain viscosity model predicts a significantly lower viscosity, with the implication of overpredicting deposit and sintering potential. The alfalfa stem biomass ash presented rather surprising behavior, as sublimation of material (presumably potassium compounds) was observed rather than any evidence of sintering. For the Rochelle and North Antelope ashes, both FACT calculations and the Urbain model using bulk ash composition predicted that large amounts of liquid phases should be present with very low viscosity at the experimental sintering temperatures.

The results of the project show that sintering is indeed physically occurring and that measurable viscosities can be obtained in the low-temperature, high-viscosity regime. Although the viscosities calculated from five sintering models were quite consistent, they were significantly higher than those predicted by the modified Urbain equation either based on bulk composition or liquid-phase composition. Further, equilibrium thermodynamic models did not predict liquid phases to exist until temperatures well above the temperatures at which sintering was observed to occur. This indicates the need for a model which will provide realistic viscosity predictions in the temperature regime where deposit sintering occurs.

It was not possible to develop practical relationships for a model of deposit sintering and strength development based on the experimental results of the project. The first obstacle is the very narrow temperature range over which sintering measurements can be made, which results in effectively obtaining a single temperature at which the viscosity is on the order of 10^7 poise and rates of sintering proceeding to completion in 30–300 seconds. The second obstacle is the lack of measured viscosities or a model such as the modified Urbain equation to predict viscosities and thus sintering rates outside this range with even moderate accuracy. Any modeling attempt would thus either be based on extrapolation of the sintering data far from the experimental measurement temperature or be based on a viscosity model not representing the actual ash behavior.

Future Work

The most pressing need is a means to obtain experimental viscosity measurements throughout the range of viscosities higher than can be measured by conventional viscometry. The method of viscosity determination by measurement of sintering rate does provide some information, but labor and instrument stability allow measurements in only a narrow viscosity range. Before an effective model of sintering strength development and deposit removability can be formulated, better knowledge of viscosity in this region is needed, with measurements being able to be easily obtained on a large number of particles over quite long time periods. The Washburn model appears to have promise in providing such viscosity information if combined with larger ash samples being periodically examined to determine the progress of sintering rather than the monitoring of single particle pairs as they are heated.

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APPENDIX A

**COMPUTED VARIABLES
FOR THE HOPPER MODEL
AND MODIFIED FRENKEL MODEL**

TABLE A-1

Computed Variables for the Hopper Model

$(\gamma t)/(\eta r_f)$	(x/r_f)
0	0
0.00135	0.00355
0.00297	0.0071
0.00860	0.0181
0.01986	0.0372
0.0331	0.0574
0.0483	0.0787
0.0656	0.1013
0.0851	0.1253
0.1071	0.1509
0.1321	0.1782
0.1604	0.2075
0.1927	0.2391
0.2299	0.2734
0.2731	0.3106
0.3239	0.3515
0.3848	0.3967
0.4595	0.4472
0.5542	0.5046
0.6809	0.5713
0.8660	0.6520
1.1946	0.7577
1.4426	0.8147
1.6417	0.8501
1.9845	0.8955
2.5839	0.9438
3.1325	0.9676
3.7342	0.9825
4.2836	0.9900
5.4348	0.9968
	1

TABLE A-2

Computed Variables for the Modified Frenkel Model	
$(\gamma t)/(\eta r_o)$	(x/r)
0.0001	0.0100
0.01	0.0979
0.02	0.1396
0.03	0.1713
0.04	0.1984
0.05	0.2210
0.06	0.2419
0.07	0.2609
0.08	0.2786
0.09	0.2949
0.10	0.3109
0.20	0.4274
0.30	0.5060
0.40	0.5736
0.50	0.6242
0.60	0.6721
0.70	0.7062
0.80	0.7403
0.90	0.7666
1.00	0.7910
1.50	0.8767
2.00	0.9241
4.00	0.9872
6.00	0.9976
8.00	0.9995