

## THERMAL PROPERTIES OF COAL ASHES

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### ABSTRACT

The applicability of differential thermal analysis to determine the fusibility behavior of coal ashes was investigated. The technique proved useful to obtain four specific temperature points. These are: the minimum sintering temperature, the softening point, the point of complete fluidity and the reaction temperature which is tentatively identified as a phase boundary crossing or eutectic temperature.

### INTRODUCTION

There is an abundance of coal in the United States, much of which is used for power generation. It is envisioned that in the future coal will be converted to "synfuel" as a replacement for crude oil. Coal in itself is a complex mixture of organic and inorganic components, together with large quantities of physically and/or chemically bound water. The inorganic component, which may amount to 15 to 20% by weight of the coal, is a complex mixture of quartz, pyrite, calcite, and silicates. Trace quantities of many metals are present. In the combustion process the coal is converted to ash, steam and other vapors.

Kiss and King [1] consider that the ash forming constituents should be classified into two groups: inorganics and minerals. The inorganic are relatively evenly distributed throughout the coal, while the minerals occur as discrete particles throughout the coal seam. The minerals are converted to ash via a pathway that includes dehydration, dehydroxylation and gas/solid phase reactions. The inorganics, which are the major ash forming species, are converted to ash via a pathway that includes coal devolatilization, burning of the solid residue (char), reduction of metal oxides, release of fly ash, sulfur, and other species, nucleation and growth of solid particles, gas phase reactions and condensation, and gas/solid phase reactions. Thus the ash material is likely to be a heterogeneous mixture of oxides, phosphates and sulfates.

In an industrial combustion process, a portion of the ash will be carried along with the stack gases. This "fly ash" may differ in composition and/or structure from the remaining "bottom ash". Ash formation is a by-product in reactions such as coal liquification. The inorganic phase itself may

influence the kinetics and the products distribution of various reactions and may have a strong bearing on the service life of the process equipment.

The ash must be removed from the process and disposed of in a safe and economic manner. Intensive research efforts are underway to find uses for ashes of various kind and to overcome the contamination of the environment by leaching from landfills and through the escape of fly ash into the atmosphere.

The efficient design of coal combustors, coal processing reactors, and ash removal systems mandates that the designer has information available on the thermal characteristics of the ash. The data base needed include: Ash fusion characteristics, heat capacities, and thermal conductivities.

The standard test to determine the fusibility behavior of coal ashes is the ASTM D-1857 "Fusibility of Coal and Coke Ash" procedure. It prescribes a preparation and measurement scheme which yields four "call" points which presumably describe the fusing process. The points are empirically defined and bear tenuous relations to actual physical phenomena.

Sintering of a powder leads to the reduction of volume and surface energy. Thus the onset of sintering, i.e. the minimum sintering or agglomeration temperature, can be determined either by dilatometry or by a technique such as differential thermal analysis (DTA).

In dilatometric experiments [2] the powder to be tested is placed into a quartz tube and piston assembly, and the sample is compressed by an adjustable load. The experimental assembly is then heated at some preselected rate and the expansion or contraction of the sample is detected by a linear variable differential transducer and recorded as a function of temperature. In general, the powder dilates on heating due to thermal expansion. Eventually, a temperature is reached where the surface of the particles begin to deform due to viscous flattening and/or sintering at the intergranular contact points resulting in contraction of the sample. The temperature at which this phenomenon occurs is the minimum sintering temperature,  $T_s$ .  $T_s$  is a characteristic for each powder and the point where particle agglomeration will first occur.

DTA indicates the onset temperature of change and the direction of change in the internal energy of a material due to heating. Reduction of surface energy is an exothermic event and will show up as such in the DTA signal. Fusion on the other hand is an endothermic event and will manifest itself as such in the DTA signal. Chemical reactions and non-ideal dissolution phenomena will show up as either increases or decreases or as slope changes in the DTA signal. In principle, besides yielding minimum sintering temperatures DTA should provide further fusibility information on ash powders. DTA experiments were performed on a set of coal ashes prepared from coals of the Argonne Premium Coal Bank and are reported here.

## EXPERIMENTAL TECHNIQUE

Ashes were prepared from eight coals. These were obtained from the Argonne Premium Coal Sample Bank [3]. In Table I the rank of the original coals and their mineral contents are listed. The ashes were prepared by combustion of 100 mesh size particles at 700°C in a muffle furnace. Part of the ashes were used for DTA measurements and elemental analysis. The rest was heated to 1000°C in a muffle furnace before being used for experiments in the DTA. Elemental analysis was performed using the inductively coupled plasma technique. Results of the elemental analysis are given in Table II. The fusion behavior of the ash powders was investigated with the use of DTA [4]. A DuPont 2100 Thermal Analyzer with a high temperature (1600°C) DTA cell was employed. The samples were heated from 300K to 1900K at the rate of 20°C/min in nitrogen flow. The instrument was calibrated using zinc and gold as standard materials.

## RESULTS AND DISCUSSION

The results of the DTA experiments on the ashes derived from the Pittsburgh #8 coal are shown in figure 1. The ordinate of the graph represents the temperature deviation of the ash sample from a baseline which corresponds to the temperature evolution of a sample not undergoing a physical or chemical transformation process.

This set of results is indicative of the results obtained for the other ashes with some variation in details. As was expected, several characteristic temperatures at which significant events occur may be identified. These points of interest, starting with the lowest temperature, are the:

- . Onset of particle agglomeration (sintering), Ts.
- . Onset of fusion (ash softening), Ti.
- . Point of discontinuous change in , Tr.
- . Point of complete fluidity, Tf.

In Table III we tabulate these temperature points for all the ashes. One should note that for a given origin ash there is only a relatively small variation in the characteristic temperatures for the ash powders prepared at different temperatures.

### The Minimum Sintering Temperature

We previously reported [2] minimum sintering temperatures for a number of coal ashes spanning the same geographic spectrum as those reported here. The method of detection employed in the prior work was dilatometry. In general, the Ts value detected by dilatometry was approximately 100K larger than that detected by DTA. We attribute much of this discrepancy to the way the DTA method was employed in these experiments. However it is important to note that both of these techniques yield a minimum sintering temperature

substantially lower than the initial deformation temperature (IDT) of the ASTM procedure. Rhinehart and Attar [5] have proposed a model for the ash fusion temperatures based on the freezing point depression equation for ideal binary solutions. They used a data base of 263 ashes to perform a seven-parameter correlation analysis. Six of the parameters are statistically determined "pseudo" heats of fusion for the assumed ash components, and the seventh is a fusion temperature for the "average composition" ash. The calculated average ash IDT is 1411K. Experimentally determined IDT's for the Argonne ashes range upwards from 1340K in a reducing atmosphere and upwards from 1445K in an oxidizing atmosphere [3]. It is clear that the IDT temperature is not a measure of the onset of agglomeration.

#### The Fusion Phenomenon

Melting is a first order phase transition phenomenon accompanied by a discontinuous increase in the enthalpy for pure homogeneous compounds. For dilute solutions the freezing point depression expression may be used to estimate the initial decrease in the freezing point of the solvent due to the addition of the non-volatile solute. Ashes are heterogeneous mixtures and certainly do not act as dilute solutions. The individual compounds which make up the ash mixture each have melting points which are higher than the most of the observed initial softening temperatures,  $T_i$ . In the sintering process melting of the powder surface occurs hence several oxides can dissolve in each other. These oxide solutions have substantially lower melting temperatures than the individual oxides. For example the melting point of an iron oxide-silica slag of composition  $Fe_2S_2O_4$  has the melting point of 1450K. Thus the initial softening temperature  $T_i$  may be considered as the melting point of the lowest melting "component" in the system. The molten component then acts as a solvent and dissolves some of the remaining solid. The dissolution process, unlikely to be ideal (i.e.  $H_{sol} = 0$ ), is accompanied by an enthalpy change. Completion of dissolution is marked by the fluidity temperature  $T_f$ . During the dissolution process one reaches eventually a point where the solution composition passes a phase boundary. Such a boundary crossing may be associated with a latent heat or may be athermal. It is our conjecture that the sharp change in  $T_i$  at the temperature which we call  $T_r$  indicates such an event. It is to be noted that in the vicinity of  $T_r$  we have the greatest variability in the nature of the DTA curves.

#### The Initial Softening temperature

The softening temperature as evaluated by Rhinehart and Attar is 1478K for the average ash. Values for the Argonne ashes, range upwards from 1365K depending on the particular ash and on the furnace atmosphere [3]. For the ash illustrated in Figure 1 we estimate that in an inert atmosphere the initial

deformation temperature, the spherical softening point and the hemispherical softening points are 1520K, 1550K, and 1580K respectively. From the  $T_i$  values as defined, we estimate that the initial softening point for a 850°C ash (ashing temperature for the ASTM test) is approximately 1375K.

#### The Discontinuous Change Temperature

Of the sixteen ashes examined, eight show only a discontinuous endothermic change in , seven show exothermic behavior in prior to the endothermic discontinuity and one ash shows no discontinuity (hence no  $T_r$ ) of any kind.  $T_r$  ranges from 1490K to 1680K. It is likely that  $T_r$  is very sensitive to both ash composition and to ashing temperature.

#### The Fluidity Temperature.

The ASTM test for fusibility defines the fluidity temperature,  $T_f$ , as the point where the test sample height has decreased to approximately 10% of its original value. We consider it to be the temperature where there is a final change in indicating the melting (or dissolution) of the last bit of solid ash. The fluidity temperature for the average ash according to the Rhinehart correlation is 1581K (1609 for low Calcium ashes). For the Pittsburgh #8 ash the measured ASTM fluidity point is 1600K in a reducing atmosphere and 1705K in an oxidizing atmosphere. The DTA  $T_f$  point is 1720K for this ash.

#### CONCLUSION

- . The DTA technique to determine the fusion behavior of ashes is convenient and yields a set of physically meaningful parameters.
- . An accurate model describing the fusion behavior of ashes, based on composition, ashing temperature, and physical structure might be possible once a more extensive experimental data set is collected.

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TABLE I - Mineral Composition of the Coals ( from [2] )

COAL	RANK	MINERAL MATTER Wt % DRY COAL	MINERAL CONTENT (as % of mineral matter)			
			QUARTZ	PYRITE	CALCITE	TOTAL CLAY
UF	HVB	15.53	10	22	7	61
WY	SUBB	8.7	23	1	5	71
ILL	HVB	18.1	19	30	10	41
PITT	HVB	10.9	16	22	5	57
POC	LVB	5.5	5	2	31	62
UT	HVB	5.3	15	9	24	52
WV	HVB	21.6	12	1	1	86
ND	LGN.	8.7	7	3	20	70

TABLE II - Elemental Composition (wt. %) of the Ashes (a)

	UF	WY	ILL	PITT	POC	UT	WV	ND
Ca	1.2	11.3	1.8	1.0	3.1	2.3	0.3	9.4
Mg	0.6	2.4	0.4	0.4	0.8	0.4	0.4	3.2
Na	0.2	1.3	0.6	0.4	1.5	2.9	0.2	5.4
Al	12.3	6.7	7.0	11.4	9.5	6.1	16.1	3.0
Fe	14.7	4.4	17.2	15.2	10.8	6.6	2.1	4.9
Si	21.9	13.9	20.0	24.1	16.7	21.9	28.0	7.9
Ti	0.6	0.7	0.4	0.7	0.8	0.5	1.2	0.2
trace (b)	0.3	1.1	0.4	0.4	0.4	0.2	0.3	1.2
S (c)	1.6	8.8	2.7	0.8	5.0	3.9	0.8	12.0
K (c)	2.2	0.7	2.4	1.7	0.5	1.0	0.8	0.8

(a) Elemental analysis was done using the inductively coupled plasma technique, courtesy of DuPont's Jackson Laboratories.

(b) Trace includes: P, Sr, V, Zn, Ba, Cr, Cu, Mn, Ni and Zr

(c) K and S were calculated from SO<sub>3</sub> and K<sub>2</sub>O values reported in the Argonne User's Handbook, sect 3.2, or estimated by interpolation.

TABLE III - Fusion Temperatures (K) for the Ashes

Ashing T	Onset of Aggl. (T <sub>a</sub> )		Onset of Fusion (T <sub>f</sub> )		Endotherm. Drop (T <sub>f</sub> )		Fluidity (T <sub>f</sub> )	
	700°C	1000°C	700°C	1000°C	700°C	1000°C	700°C	1000°C
UF	900	1150	1250	1380	1675	1650	1725	1580
WY	950	950	1350	1400	1500	1490	1675	1675
ILL	950	950	1280	1440	1520	1620	1700	1540
PIT	925	950	1130	1450	1680	1660	1700	1740
POC	875	975	1350	1450	1525	1600	1650	1650
UT	975	1000	1400	1380	1620	--	1700	1650
WV	1000	1100	1400	1480	1600	--	1800	1800
ND	950	1150	1325	1375	1590	1625	1650	1640

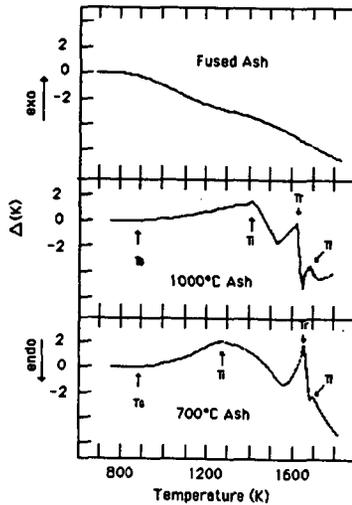


Figure 1 Differential Thermal Analysis of Pittsburgh #8 Ash