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Full Length Article

Sintering and collapse of synthetic coal ash and slag cones as observed through constant heating rate optical dilatometry☆

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ABSTRACT

Ash agglomeration and slagging are responsible for costly maintenance problems in coal-fired boilers. Boiler design and operation rely on critical ash fusion temperatures defined by geometric criteria that explicitly ignore shrinkage or warping. Reproducibility of ash fusion test (AFT) results is known to be a major problem, given the subjective nature of some criteria used in critical temperature reporting. Decades of faulty predictions based on AFT data underscore the need for an objective measure of the likelihood for agglomeration and slagging as a function of coal ash composition and temperature. Heating microscopes and ash fusibility determinators are AFT instruments that are widely available and readily adapted for optical dilatometry of ash cones through digital image analysis. Optical dilatometry enables the continuous measurement of cone height and face area, and the calculation of changes in cone volume and density as a function of temperature during constant heating. A strong correlation was found between the sintering onset temperatures of two synthetic ash compositions measured through optical dilatometry and their corresponding solidus temperatures predicted through thermophysical modeling. The sintering onset temperatures of synthetic slag cones appears consistent with glass transition temperatures estimated using the Kauzmann-Beaman rule. Cone collapse is highly correlated with softening, hemispherical, and fluid temperatures for ash cones. Rapid changes in solid, liquid, and gas volume fractions near the collapse temperature suggest that a transition from capillary to slurry state may play an important role in triggering collapse. Slag cone collapse is better explained by a decrease in viscosity as a function of temperature in the glass working range. The sintering onset temperature and cone collapse temperature are readily understood through thermophysical modeling based on ash composition and provide two additional critical temperatures in the modeling of coal ash agglomeration and slagging.

1. Introduction

Coal ash, a mixture of incombustible minerals and biomass-derived inorganic compounds, can agglomerate into clinkers or fuse into molten slags during coal combustion [1]. The ash fusion temperature (AFT) test was devised nearly a century ago as a way of predicting clinkering in coal-fired stoker furnaces [2]. It remains widely used today as the basis for estimating coal ash fusibility and slag critical viscosity in coal combustion and gasification [3]. In an AFT test, coal ash cones are heated at a constant rate while an observer records critical temperatures at which the cones meet specific deformation criteria. For instance, four critical temperatures are defined by the ASTM D1857 AFT test [4]. First, the initial deformation temperature (IDT) is defined as the temperature at which the sharp tip of the coal ash cone becomes rounded. Next, the softening temperature (ST) is the temperature at which the cone height is equal to its width. Thirdly, the hemispherical temperature (HT) is the temperature at which the cone width is equal to twice its height. Lastly, the fluid temperature (FT) is the temperature at which the cone has melted down to a flat layer with a maximum height of 1.6 mm (1/16 in). Similar AFT critical temperature criteria may be found in international (e.g. ISO 540) and national standards (e.g. BS 1016-15, DD CEN/TS 15370, DIN 51730, JIS M 8801, GB/T 219, and GOST 2057).

AFT critical temperatures constitute the basis for several coal boiler design parameters and operating guidelines: the furnace exit gas temperature index (based on IDT and ST), the slagging index (IDT and HT), furnace tube deposits slagging or fouling index (IDT and FT), as well as the propensity for the coal ash to adhere to metal surfaces at temperatures above ST [5–7]. As a result, much data on coal ash compositions and associated critical temperatures have been published for

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Table 1
Synthetic coal ash compositions (%, mass/mass), values may not add up to 100% due to rounding. Corresponding slag compositions were verified based on wavelength dispersive X-ray spectroscopy [26]. Bulk slag densities (ρ) and expanded uncertainties (coverage factor k = 2, which approximates 95% coverage of the true measurand value) are given to the right of their respective compositions. See text for discussion of the ambient temperature density measurements.

sample number	SiO_2 %	Al_2O_3 %	CaO %	MgO %	Na_2O %	K_2O %	TiO_2 %	Fe_2O_3 %	ρ (g/cm^3)	U(ρ) (g/cm^3)
1	40.8	20.4	0.6	0.8	0.35	2.45	0.8	32.6	2.92	0.06
2	38.1	25.4	2.6	0.7	0.3	1.6	1.0	27.5	2.71	0.11
3	36.7	29.3	0.9	0.3	0.1	0.7	0.7	31.4	2.86	0.14
4	35.7	20.4	2.0	0.5	0.2	1.6	0.9	36.7	3.07	0.15
5	44.8	24.0	1.0	0.6	0.1	1.5	1.0	27.1	2.90	0.15
6	45.1	20.5	1.1	0.7	0.1	2.5	1.3	28.7	2.86	0.14
7	49.6	26.3	2.1	1.1	0.64	2.4	1.2	15.4	2.67	0.12

coals mined across the world. Nonetheless, decades of large boiler design and operation have shown that reliance on AFT data can result in both false positive and false negative results [8]. In light of these costly mistakes, the ASME Ash Fusion Research Project noted the need for "replacement techniques…that both remove the operator subjectivity inherent in ash fusion measurement and more closely reflect the conditions and processes that contribute to the slagging mechanism [5]."

Formation of a low-melting point slag often precedes the formation of strongly-sintered coal ash deposits on heat-transfer surfaces in coal-fired boilers [9]. Prior studies have shown that the coal ash solidus temperature, or the temperature at which a molten slag phase begins to form, is lower than the IDT [10], sometimes by over 100 °C [11]. In addition, agglomeration of coal minerals in fluidized beds occurs when particles become cohesive due to the formation of a molten phase [12]. Numerous experimental methods have been evaluated as replacement techniques for the AFT test in predicting the sintering and slagging characteristics of coal ashes, including the measurement of electrical resistance at the onset of sintering [9,10,13], simultaneous thermogravimetric analysis and differential scanning calorimetry to detect the endothermic reaction during melting [11], thermomechanical analysis of changes in sample dimension under mechanical loading as a function of temperature [10,14–18], measurement of change in gas pressure flowing through a porous sample at constant temperature [19] or during constant heating [20], and optical dilatometry with constant heating [21–23]. Of these methods, optical dilatometry shares the greatest similarities to conventional AFT tests performed with heating microscopes and ash fusibility determinators (i.e. controlled-atmosphere analytical furnaces fitted with long-distance microscopes).

Dilatometry is a technique that quantifies the change in sample length or volume as a function of temperature. Instruments may be characterized by contact versus noncontact measurement methods. Thermomechanical analyzers and push-rod dilatometers apply an external force to the sample through direct physical contact and measure mechanical displacement as a function of temperature. In contrast, changes in sample dimensions are measured in optical dilatometers without direct physical contact; consequently, dilatometry samples are not subject to external forces other than gravity. Optical dilatometry has been applied to the study of mineral phase transformations due to sintering and crystallization [24].

Heating microscopes and ash fusibility determinators are readily adapted to making optical dilatometry measurements of coal ash sintering through the analysis of digital imagery data. Commercially available instruments typically implement proprietary image processing algorithms to remove operator subjectivity in ash fusion temperature measurements. The present study implements an image processing algorithm with public domain software to measure sintering-induced changes in cone height and volume for two synthetic coal ashes and seven synthetic coal ash slags using digital imagery collected during ASTM D1857 AFT measurements. In addition, CALPHAD (CALculation of PHAse Diagrams) thermophysical modeling was used to calculate the solid and liquid (molten slag) fractions present in the synthetic coal ash as a function of temperature [25]. Together, the optical profilometry and thermophysical modeling provide a new perspective on the phase transformations taking place during a typical AFT test. A better understanding of the physical and chemical processes occurring during AFT testing is necessary to improve the modeling of coal ash agglomeration and slagging processes in coal boilers and gasifiers.

2. Material and methods

2.1. Synthetic coal ash and slag preparation and characterization

The method of preparing the synthetic coal ash and slag used in this study was described in a previous paper [26]; consequently, only a brief summary will be provided to provide context. Commercially procured minerals and chemically pure oxides were used as the starting materials for the synthetic coal ashes. Mixtures of olivine, potash feldspar, silica, iron oxide, wollastonite, and alumina were ball milled together for 6 h for all synthetic coal ashes except sample 7. Dolomite, potash feldspar, and silica were combined in a tubular mixer to create the mixture for sample 7. Red mica, kaolin, magnesium oxide, and iron oxide were then added to each synthetic coal ash mixture to yield the compositions specified in Table 1. A subset of the samples was prepared by calcining the red mica, kaolin, and magnesium oxide separately at 800 °C for 4–6 h in air. The resultant mixtures were then ball milled again for 6 h. Milled powder uniformity was verified with smear tests, and sample compositions were verified using wavelength dispersive x-ray spectroscopy.

Synthetic coal ash slag samples were prepared by melting each synthetic coal ash separately in high-density alumina crucibles at temperatures ranging from 1400 to 1535 °C. The synthetic slags were mechanically separated from the crucibles after cooling. Bulk slag densities were measured using Archimedes' principle, using deionized water as the working fluid. The slags were crushed and ground into irregular particles with diameters less than 2 mm. The slag particles were further reduced to a fine powder with a shatterbox.

A dextrin solution (10.6% mass/mass) was used in the fabrication of the synthetic coal ash and slag cones. Either coal ash or slag powders were mixed with the dextrin solution and pressed into a mold to form triangular pyramids that are 1.9 cm (0.75 in) in height and 0.64 cm (0.25 in) wide at the base. Ash and slag cones were air-dried, and then mounted on a prefabricated kaolin-alumina base with an alumina-based cement. Air-dried cone masses were measured with an analytical balance. The cones were air-dried again and ignited to remove organic matter prior to testing.

2.2. High-temperature optical dilatometry

Ash and slag cone samples were heated at 8.7 °C/min, with an expanded uncertainty of 0.8 °C/min, under a reducing atmosphere (0.799 standard liters per minute CO_2 and 1.200 slpm CO, with an expanded uncertainty of 0.007 slpm for both gases) to 1500 °C in a commercial ash fusibility determinator (LECO AF700). Estimated standard