RHEOLOGICAL CHARACTERISATION OF COAL ASH AT HIGH TEMPERATURES

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ABSTRACT

A good knowledge of the rheological behaviour of coal ash deposit at high temperatures and under the actual processing conditions is important for understanding the mechanisms of agglomeration phenomena in fluidised-bed combustion and gasification processes for low-rank coals. Rheological characterisation of materials at high temperatures is difficult due to a lack of standard instruments and reliable measurement techniques. We have recently developed a specially designed rheometer that has the capability of measuring the absolute rheological properties of coal ash deposits over a wide range of high temperatures and processing conditions. In this paper, the features of this unique instrument are described and the experimental technique developed for flow property measurement is outlined. Some typical rheological properties measured for coal ash deposits from different Australian low-rank coals are presented and discussed to illustrate the usefulness of the rheometer for high-temperature rheological characterisation.

INTRODUCTION

Agglomeration of bed materials caused by ash deposition is potentially a problem in fluidised bed combustion and fluidised bed gasification of low-rank coals. Successful operations of these systems will depend on the ability to control ash deposition and agglomeration and to prevent defluidisation of bed materials. Recent studies on fluidised bed combustion [1,2] have suggested that the deposition of ash is caused by the transfer of molten mineral matter from the burning char particles onto the surface of bed material upon collision of char and bed particles. Further collisions among the bed particles, coated with a sticky layer of partially molten ash, would result in agglomeration of the bed material. Consequently, the large agglomerates of bed particles would ultimately lead to defluidisation of the bed at the operating fluidising velocity. Two possible mechanisms for particle agglomeration in fluid-bed combustion may be relevant to low-rank coal [1]. In the first mechanism, partial melting or reactive liquid sintering, ash with high sodium, chlorine and sulphur contents may form low-melting point eutectics, which partially melt at low bed temperatures, ca. 500-700^{o}C. The presence of the liquid phase makes the ash 'sticky' and would facilitate the transfer and adhesion of ash to the bed particles. The amount of the molten phase controls the stickiness of the ash-coated particles and determines the tendency for particles to agglomerate contact by collision. The second mechanism, viscous flow sintering, involves melting of ash at temperatures greater than 1000^{o}C, producing a highly viscous liquid phase, which controls the sintering process. The high viscosity of the molten ash may keep the liquid in the glassy phase when the ash is deposited onto the bed particle surface whose temperature is normally lower than that of the char particles. Viscous flow sintering appears to be predominant in ash with a high silica content [1]. It is a time-dependent process and the molten ash viscosity has been demonstrated to control neck formation in sintered particles [3]. The mechanisms for agglomeration and defluidisation in fluidised bed gasification may be somewhat different and directly involve the char particles under the reduced furnace condition, higher operating temperatures and different bed characteristics.

An understanding of the specific mechanisms involved in agglomeration and defluidisation in fluidised bed processing of low-rank coal requires a good knowledge of the intrinsic physical properties of the molten coal ash as a function of the operating conditions, coal types and chemical and mineral compositions of the ash deposit. The rheological properties of the coal ash formed under furnace condition are important in controlling the stickiness and mobility of the molten ash depositing onto bed and char particles. At present, there are no reliable techniques for measuring the absolute rheological properties of coal ash under the temperature and furnace conditions of interest. The available high-temperature viscometers either use non-standard geometries or merely provide single-point measurements assuming that molten coal ash behaves as a Newtonian liquid [4-6]. This paper reports on the development of a recently constructed high-temperature ash rheometer which was designed based on the principles of viscometric flows and is capable of characterising the rheology of coal ash over a wide range of temperature and operating condition. Some experimental results obtained for different coal-ash samples from Australian low-rank coals are presented to demonstrate the suitability of the rheometer for high-temperature rheological measurements.

THE HIGH-TEMPERATURE ASH RHEOMETER

Design Features

The ash rheometer constructed in this research has been designed for direct measurement of the rheological properties of coal ash under a controlled environment at temperatures of between 500^{o}C and 1300^{o}C, which are typical conditions in the combustion, and gasification of low-rank coal. As shown schematically in Fig. 1, the instrument employs the cone and plate principle for rheological measurements which involve shearing a volume of molten ash sample contained in a thin gap between a flat plate and a small-angle cone. The flat plate, which also acts as a crucible containing the sample, can be rotated under controlled angular speeds. The major advantage of the cone-plate geometry as compared to the conventional concentric cylindrical system used in many other high-temperature viscometers is that the shear rate within the sample is uniform and well defined in the former whereas it may vary significantly in the annulus of the latter configuration [7]. Other advantages of the cone-plate system include a small volume of ash sample required for testing, ease in sample loading, heating and in temperature control, and minimum errors arising due to end and wall effects of the instrument. The cone-plate system is constructed of a special alloy that can withstand the high temperature and reactive environment while in direct contact with the molten ash with any chemical and mineral characteristics. The sensor system containing the test sample is totally enclosed in a vertical tube furnace equipped with a microprocessor temperature controller capable of providing a constant temperature of up to 1300^{o}C. The completely sealed cylindrical chamber within the furnace allows the testing environment to be fully controlled under neutral, oxidising or reducing condition. Temperature of the ash sample in the hot zone is measured using a type-K thermocouple. Primary measurable variables are the torque acting of the stationary cone as a function of the plate rotational speed from which the shear stress versus shear rate data, which defines the shear rheological behaviour of a fluid, can be determined directly without the need for calibration. The high sensitivity and resolution that are typical of any commercial rheometer are another feature of the ash rheometer. Interchangeable torsion bars coupled with a Linear Variable Differential Transducer (LVDT) are employed to measure the torque over a significantly wide range of 0.003 to 45Nm. The plate is driven by an AC servomotor equipped with a programmable controller to deliver constant speeds as required. A data logger collects and stores the data into a dedicated personal computer for on-line processing and analysis.

Experimental Procedure for Rheological Measurement

Rheological measurements of the coal-ash at high temperatures are carried out using the following procedure. First, the measuring system together with the upper and lower shafts are preheated to a desired temperature in order to correctly set a zero gap setting between the cone and the plate. The zero gap is next determined and marked on a gap regulator after the measuring system has reached a thermal equilibrium state for at least one hour. This enables the materials of the measuring system and shafts to be fully expanded at the test temperature. The cone is then raised by the gap regulator and the appropriate amount of dry coal-ash sample is loaded into the plate. A desired gas (neutral, reducing or oxidising) is introduced into the furnace chamber to control the test environment. The sample is then heated to the test temperature, and heating continues at this temperature for one hour to ensure the whole sample in the hot zone reaches a thermal equilibrium state. The cone is next lowered to a preset gap and the sample is allowed to stand for half an hour to eliminate any stress in the sample due to loading. Testing commences by rotating the plate at a low and constant speed and measuring the torque acting on the cone. The rotational speed is then increased in steps and the torque response at each constant speed is recorded.

Testing with Standard and Reference Materials

Standard Materials

Once the rheometer has been constructed and commissioned, it was first tested using various standard viscous fluids with known properties to ascertain its accuracy and reliability as a high-temperature rheological instrument. Typical results for a certified standard borosilicate glass (Corning Inc.), which is commonly used as a reference material for high-temperature viscosity measurements, are shown in Figure 2 in the form of shear stress versus shear rate plots. Over the test temperature range of 840°C to 920°C, where the glass material is completely molten, the observed rheological flow curves are linear and pass through the origin. This behaviour is typical of Newtonian fluids whose viscosity is dependent on temperature only. In Figure 3, the viscosity determined from the slopes of the linear shear stress-shear rate flow curves is plotted as a function temperature and compared with the certified standard viscosity data. It may be seen that the agreement between the viscosity data obtained using the ash rheometer and the reference viscosity is excellent, with a maximum error of ±3%.

Ternary Oxide Melt

A ternary oxide melt, composed of 38% CaO, 20% Al_2O_3 and 42%SiO_2, for which viscosity data are available in the literature, has also been prepared and tested using the ash rheometer. Figure 4 shows the experimental shear stress-shear rate data for the melt as a function of temperature ranging from 1100^{o}C to 1300^{o}C. The results indicate that this oxide melt is Newtonian over the range of temperature tested. In Figure 5, the measured viscosity data are compared with the published data for the melt from other studies over a higher temperature range of 1300°C to 1600°C [8-9]. The agreement between the data from this work and the literature data is excellent, as demonstrated by the fact that and all the data can be fitted by a single Arrhenius-type model for the viscosity-temperature relationship over the whole temperature range of 1100°C to 1600°C.

RHEOLOGICAL PROPERTIES OF COAL ASH

A variety of low-rank coal ash deposits have been tested using the high-temperature ash rheometer developed in this work. Here we present typical results obtained for two ash samples from different sources. The first ash sample, from a lignite from Bowmans (South Australia), was prepared by burning the coal in a laboratory muffle furnace at 815°C for 1 hour, following the standard ashing procedure. The major components of the Bowmans coal ash are SiO_2 (11.2%), Al_2O_3 (12.3%), Fe_2O_3 (10.2%), CaO (12.6%), MgO (11.0%), and Na_2O (9.3%). The ash melts at temperature of about 900°C. The second sample is a boiler coal ash deposit obtained from a conventional power station using a Victorian brown coal. This coal ash is a mixed sulphate containing predominantly calcium and sodium sulphates which starts melting at 850°C and became fully molten at temperatures above 930°C.

Experimental rheological results obtained with the Bowmans coal ash tested at temperatures of 920°C, 1020°C and 1120°C and under a controlled inert (N_2) atmosphere are shown in Figure 6. The non-linear characteristics of the flow curves indicate that the ash sample is non-Newtonian in the range of temperature indicated. The behaviour shown is typical of a viscoplastic fluid characterised by a yield stress, which is the minimum shear stress required to start flow. The data in Figure 6 can be well correlated using the Bingham plastic model. Furthermore, as shown in Figure 7, the viscosity of this coal ash at any given temperature is not constant but decreases strongly with increasing shear rate. This behaviour, known as "shear-thinning", is commonly observed with polymer melts and particulate suspensions. At any given shear rate, the ash viscosity decreases with increasing temperature as expected.

The rheological properties of the Victorian coal ash measured under nitrogen-gas atmosphere at temperatures of 890°C, 930°C and 990°C are shown in Figure 8. This ash sample may also be characterised as viscoplastic with a yield stress, and shear-thinning with a viscosity that decreases with increasing shear rate and increasing temperature. The flow property data in Figure 8 can be satisfactorily fitted to the Casson model.

Figure 9 shows a comparison in the rheological behaviour of the Victorian coal ash deposit tested under two different furnace conditions: neutral and oxidising. It is found that, at the same temperature, the ash in an oxidising environment becomes more viscous with little or no yield stress compared to that under a neutral atmosphere. This result may be used to illustrate the significant effect of the processing environment on the rheological behaviour of coal ash with an important implication on the agglomeration tendency of the bed materials or char particles.

Comparing the results obtained for the two ash samples from different low-rank coals with different mineral characteristics and compositions, their rheological behaviour over the different ranges of temperatures tested is remarkably similar. As the testing temperatures are in the neighbourhood of the melting points, it is reasonable to assume that the physical state of the ash material is that of a concentrated suspension of ash particles imbeded in a highly viscous molten liquid, the proportion of which increases with increasing temperature. The presence of the unmelted solid ash particles and their interactions give rise to structure-like behaviour which is responsible to the observed non Newtonian flow behaviour, characterised by a yield stress and shear rate dependent viscosity. The presence of a high yield stress of the ash in the range of temperature of interest may have a significant impact on fluidised bed processing of low-rank coals. Since the yield stress is the critical shear stress that must be overcome to start viscous flow, its magnitude determines the tendency of the molten ash to adhere to the surface of bed particles following the transfer of the ash from the burning char. It is thus desirable to have a lower yield stress in order to reduce the degree of "stickiness" of molten ash matter depositing on a solid surface. Furthermore, the shear-thinning characteristic of the molten ash implies that the viscosity of coal ash deposits changes with the local particle and gas velocities in a fluidised bed. Thus, the non-Newtonian nature of molten coal ash would complicate the modelling of particle agglomeration but a good knowledge of the rheology will improve our understanding of the mechanisms of ash deposit and subsequent particle agglomeration and bed defluidisation.

CONCLUSIONS

The ash rheometer developed is unique in that it is designed based on the principles of viscometric flow for measuring the rheological behaviour of low-rank coal ash at high temperatures and under controlled environments relevant to fluidised bed processing of low-rank coals. Extensive testing of the rheometer using standard and reference materials have established the suitability and accuracy of the instrument for absolute rheological measurements at high-temperatures, without using any calibrations. Results obtained with some typical Australian low-rank coal ashes have indicated that in the operating temperature ranges of fluidised bed combustion and gasification, the ash behaves as a non-Newtonian fluid characterised by a yield stress and shear-thinning viscous behaviour. A good knowledge of the rheology of the coal ash deposit is useful for understanding the mechanisms involved in, and developing methods for controlling, agglomeration of bed particles and defluidisation of fluidised beds used for low-rank coal utilisation.

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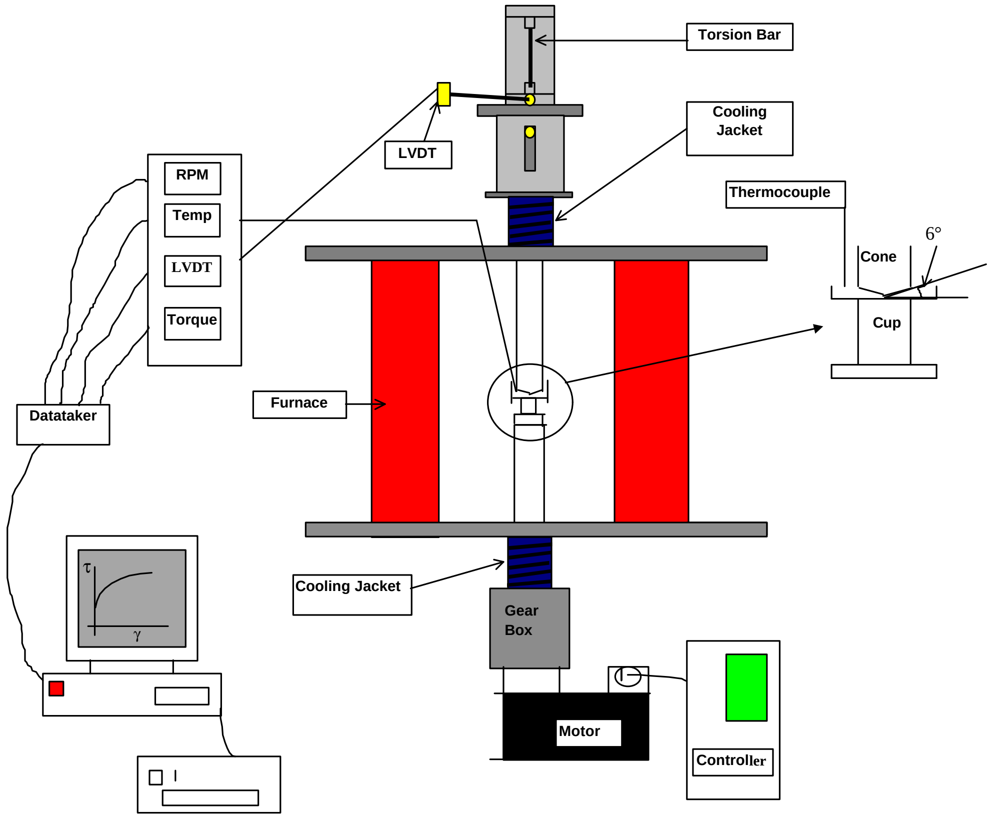

Figure 1: Schematic diagram of the ash rheometer rig

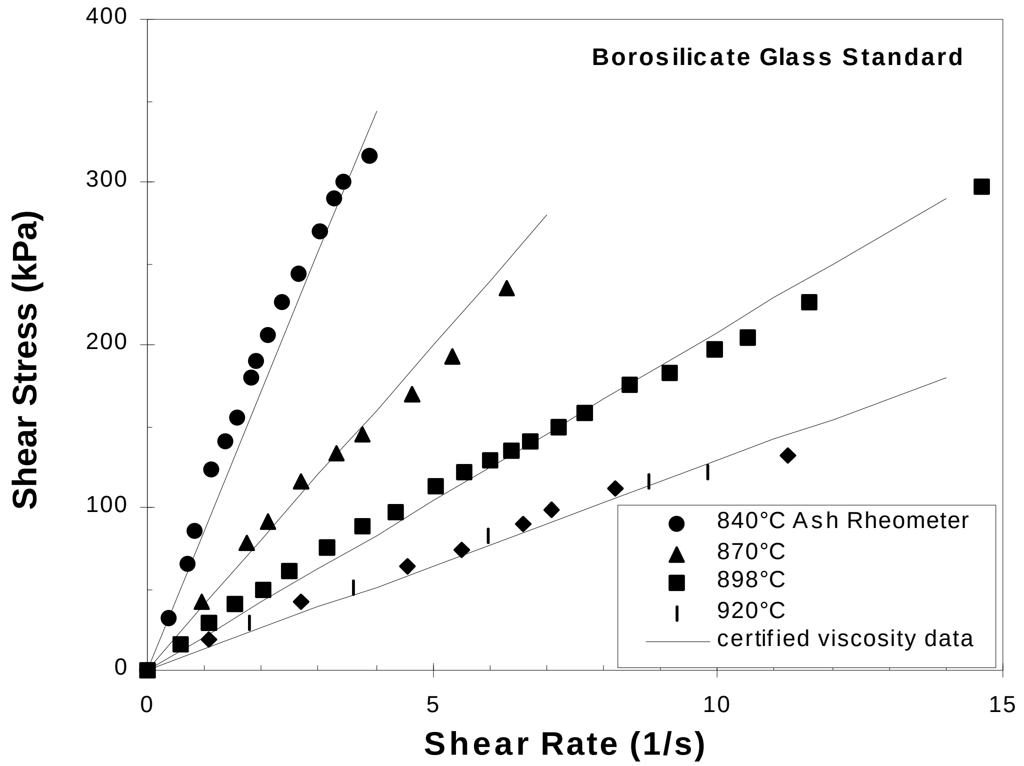

Figure 2: Experimental flow curves for borosilicate glass standard as function of temperature.

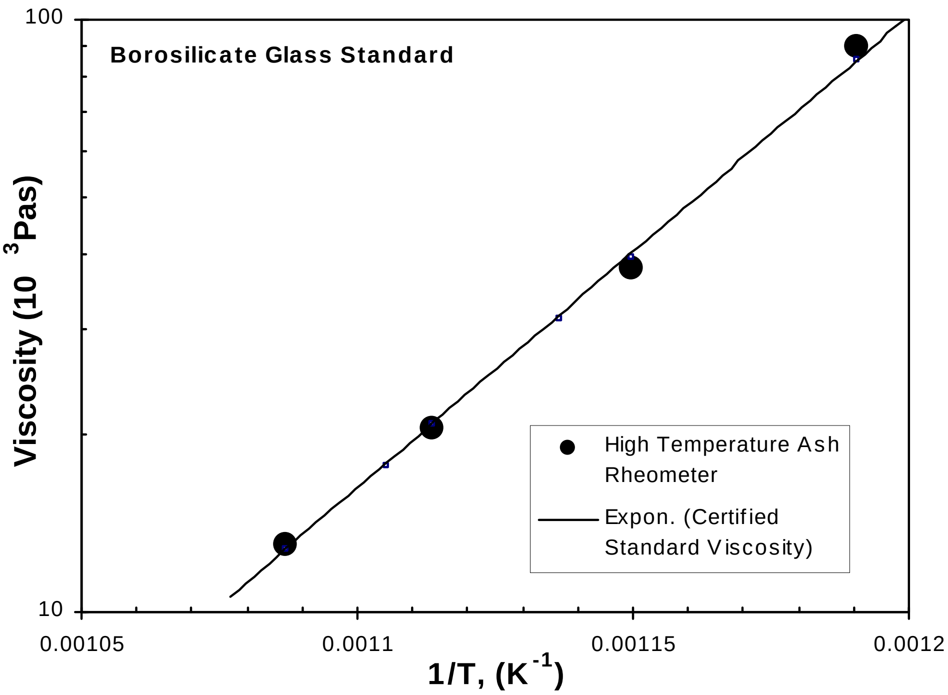

Figure 3: Comparison between measured viscosity and standard data for borosilicate glass standard.

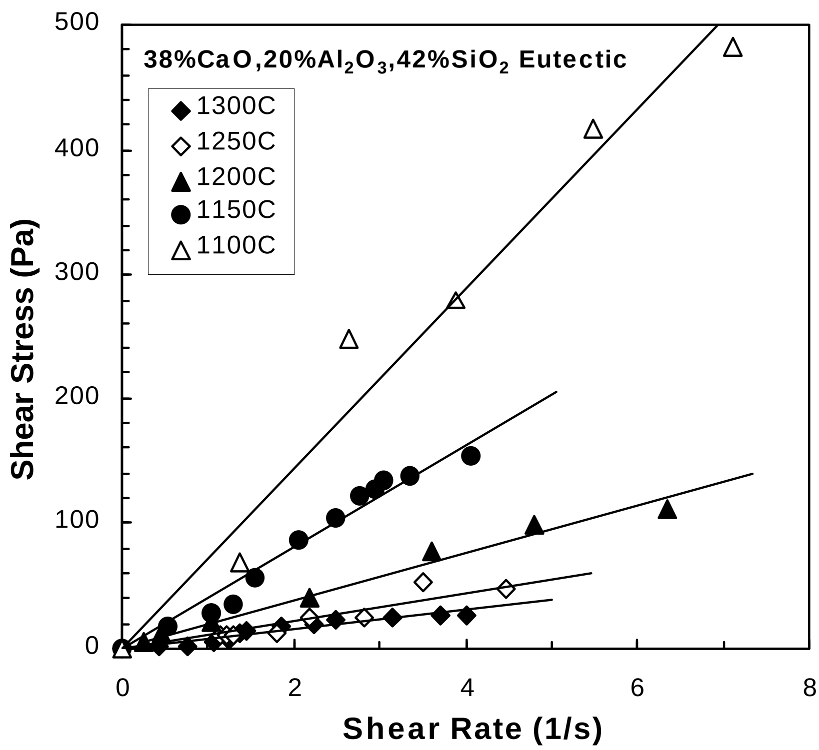

Figure 4: Experimental flow curves for a ternary oxide melt.

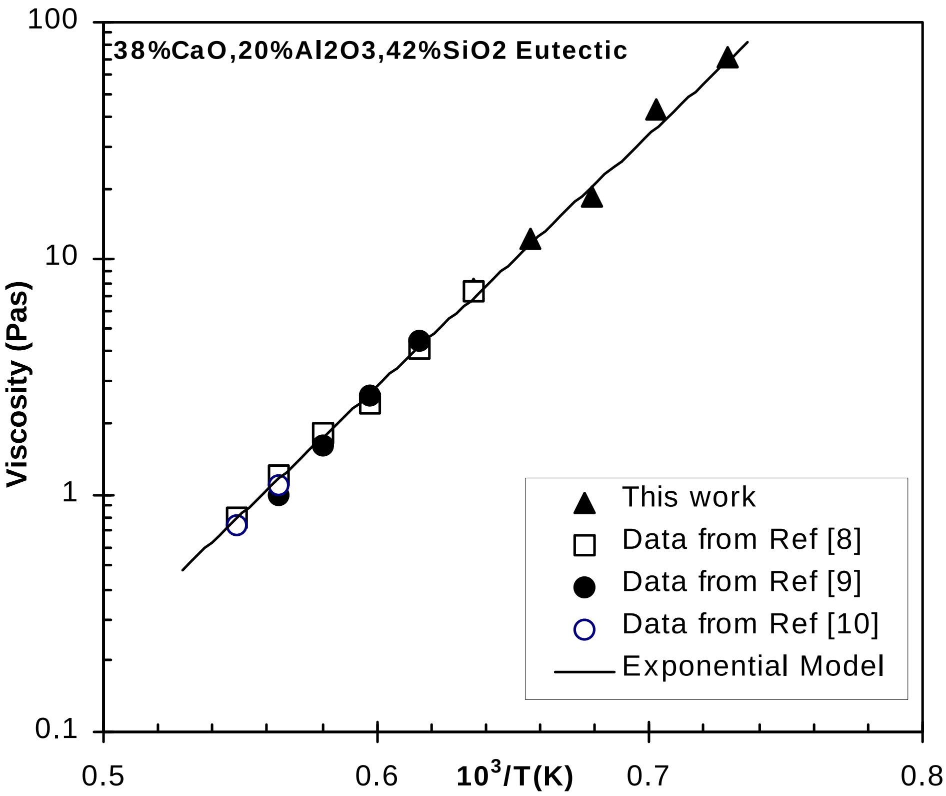

Figure 5: Comparison between measured viscosity and reference data for a ternary oxide melt.

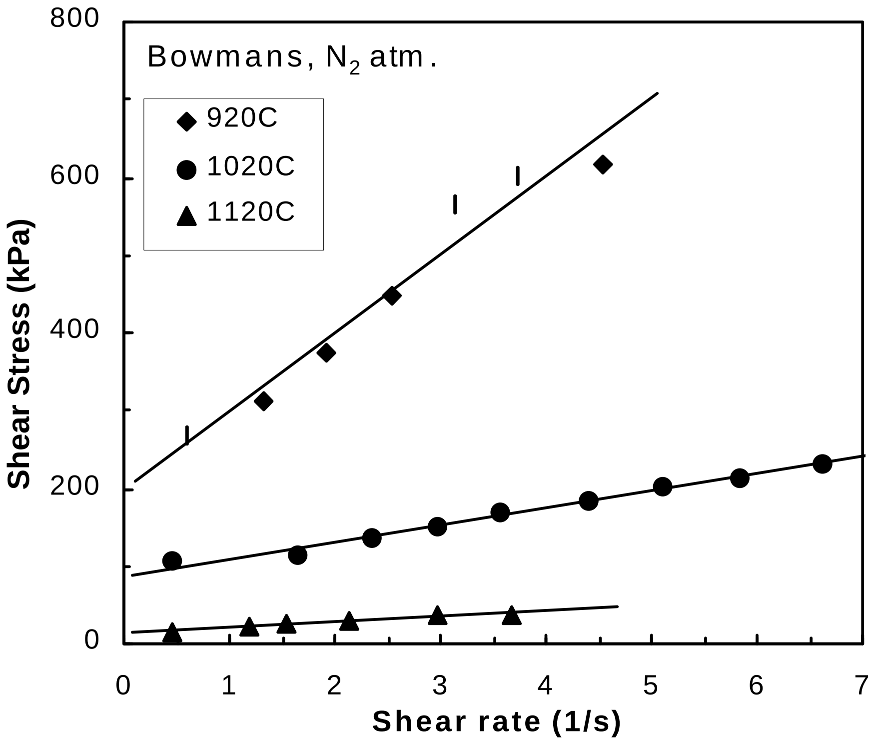

Figure 6: Flow curves for a South Australian coal ash at different temperatures.

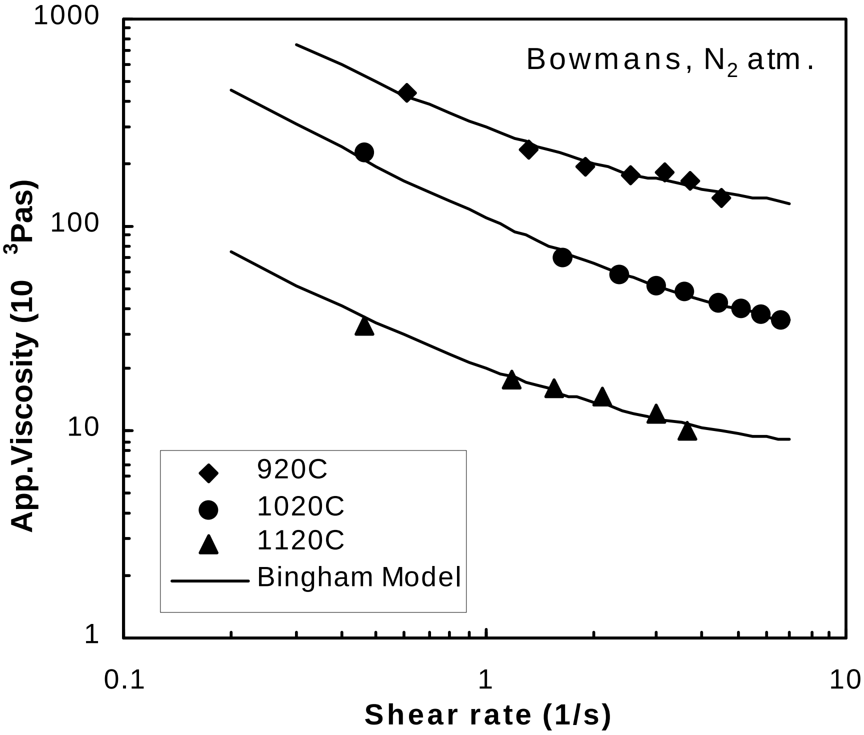

Figure 7: Apparent viscosity of a SA coal ash as a function of shear rate and temperature.

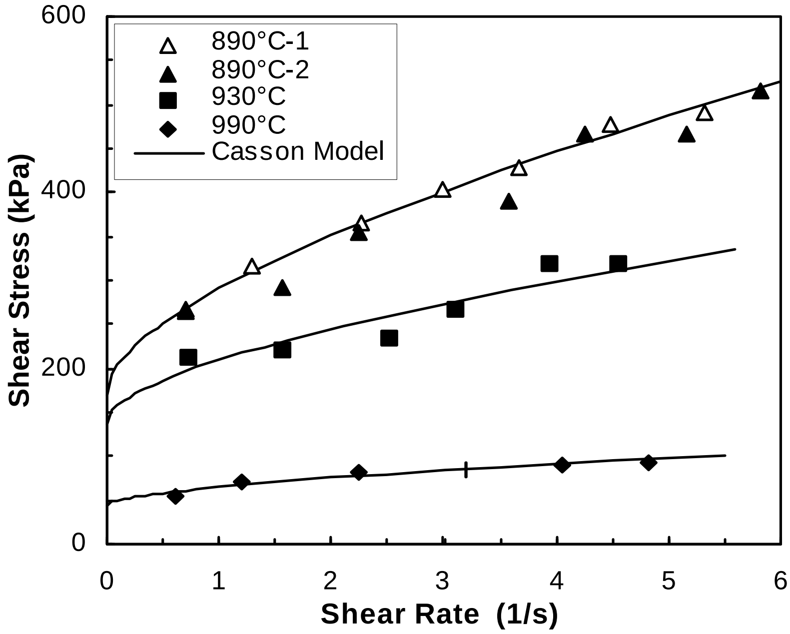

Figure 8: Flow curves for a Victorian coal ash as a function of temperature

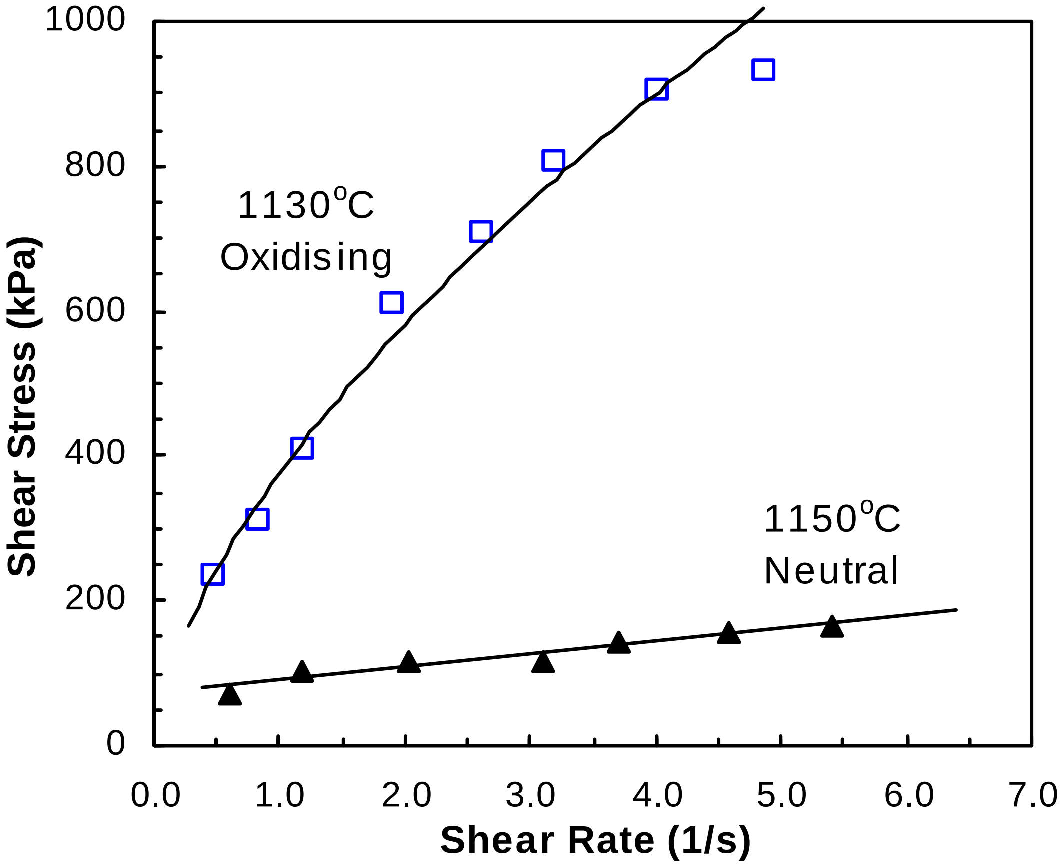

Figure 9: Effect of processing environment on rheology of a Victorian coal ash