The effect of temperature on the extrusion behavior of a polymer/ceramic refractory paste

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The effect of temperature on the extrusion behavior of a polymer/ceramic refractory paste, known as taphole clay, has been investigated. Experiments were performed to determine the extrusion pressure and the viscosity of the paste's phenolic resin binder between 30 and 60°C. The extrusion parameters were determined using the Benbow and Bridgwater method [1]. As the temperature was increased, a decrease in the extrusion pressure was observed. Three of the four Benbow and Bridgwater extrusion parameters were found to be dependent on temperature and the binder's viscosity. From this data a model was produced using a modified Benbow and Bridgwater equation that predicts the effect of temperature on the extrusion pressure of the paste.

1. Introduction

Extrusion is an important process widely used in the ceramic, pharmaceutical, polymer, metallurgical and food industries [1–5]. The temperature of the extrusion process has a large influence on the properties of the extrudate, particularly when the process involves unavoidable exposure to large temperature fluctuations. An example of this circumstance is the extrusion of taphole clay into an iron making blast furnace. Taphole clay is a polymer/ceramic composite refractory paste. It is extruded into the taphole of a blast furnace using a ram extruder (known as a mud gun) where it hardens and stops molten material escaping the furnace. Given the high temperatures of the blast furnace and the critical timing of the process, significant temperature variations can occur within the mud gun. Variability in the extrusion process can lead to variation in the performance of the taphole clay extrudate within the blast furnace, which in turn may be detrimental to several aspects of blast furnace performance.

Paste flow during ram extrusion can be divided into two areas, the flow from the barrel into the die, and the flow through the die. A schematic representation of a simple ram extruder is shown in Fig. 1. The flow from the barrel and into the die is generally differential laminar flow involving shear forces throughout the bulk of the paste. Paste flow in the die is generally described as plug flow, with the slippage occurring in a liquid layer at the die walls [3, 6]. If this is the case, the majority of the paste will not be subjected to shear stresses in the die. The entire shear will occur in the liquid binder layer at the die wall. This behaviour is often described as the "wall effect". Plug flow is believed to occur in the die because the yield stress of the paste is usually greater than the friction at the die wall. In such cases, the flow in the die is controlled by the rheology of the binder. However, when Benbow *et al.* [7] examined the behaviour of the pastes at the die wall, they found it was not entirely dominated by liquid binder rheology. They increased the percentage of binder present, which they believed would result in an increase the size of the liquid binder layer. When the binder's shear stress was constant with shear rate Benbow *et al.* [7] found the paste's shear stress was not constant as the percentage of liquid was increased. In fact, a reduction in the shear stress of the paste was found to occur. This deviation implied that not all the shearing was occurring in a liquid layer on the surface of the die wall, but in fact that some flow was occurring in the paste.

Even when the shear flow occurs within the body of the paste and at the die walls, the rheology of the binder will still have a considerable influence. The temperature of extrusion affects the binder's viscosity and hence has a significant effect on the flow through the die and the shear stress in the bulk of the paste as it is extruded from the barrel into the die.

Equation 1 was developed by Benbow and Bridgwater to examine the pressure drop across a ram extruder. Many authors have used this model to examine the extrusion behaviour of ceramic pastes, but it has also been applied to foods and soaps [1–3, 5, 8].

$$P = 2(\sigma_0 + \alpha V)\ln\frac{D_0}{D} + 4(\tau_0 + \beta V)\left(\frac{L}{D}\right) \quad (1)$$

P is the pressure drop across the extruder, V is the velocity of the extrudate exiting the die, D_0 is the diameter of the barrel, D is the diameter of the die land, and L is the length of the die. The first part of the equation is concerned with the energy required to force the material from the barrel into the die. Benbow and Bridgwater describe the factor $(\sigma_0 + \alpha V)$ as being the bulk yield stress corrected for shear rate. The individual factors are the yield stress of the paste at zero velocity, σ_0, and the factor that characterizes the effect of velocity on the

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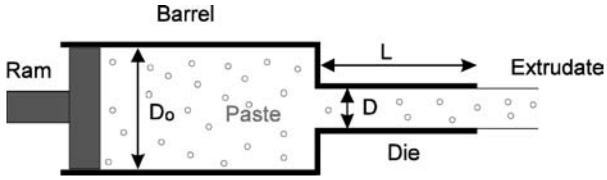

Figure 1 Schematic representation of the cross section of the basic elements of a ram extruder.

paste, α. The second part of the equation concerns the flow of the paste through the die. The wall shear stress at zero velocity is τ_0, the initial wall stress. The factor that accounts for the effect of velocity on the wall shear stress is β termed the wall velocity factor. This equation does not account for flow of material in the barrel.

Benbow and Bridgwater also observed non-linear behaviour of the pastes. The more generalised non-linear equation is given in Equation 2. The parameters m, and n allow for the nonlinearity attributed to the effect of extrusion speed on α and β.

$$P = 2(\sigma_0 + \alpha V^{\mathrm{m}}) \ln \frac{D_0}{D} + 4(\tau_0 + \beta V^{\mathrm{n}}) \left(\frac{L}{D}\right) \tag{2}$$

Zheng *et al.* [9] have examined the Benbow-Bridgwater equation with respect to relating the initial differential laminar flow from the barrel into the die to the paste characteristics. They determined that the Benbow-Bridgwater bulk yield stress could be related to the Herschel-Bulkey equation [10] for paste flow. The Herschel-Bulkey equation describes the flow of slurries and pastes that exhibit a yield stress (Equation 3) [10]. In Equation 3, τ is the shear stress, τ_y is the yield stress, K is the Herschel-Bulkley shear rate factor, $\dot{\gamma}$ is the shear rate and m_{HB} is the Herschel-Bulkley flow behaviour index.

$$\tau = \tau_{\mathrm{y}} + K\dot{\gamma}^{\mathrm{m_{HB}}} \tag{3}$$

Zheng *et al.* developed the equation for the extrusion pressure due to the bulk yield stress that accounted for different die diameter sizes and then incorporated the Herschel-Bulkey equation (Equation 4). This study showed that it is possible to link the Benbow-Bridgwater equation to the material properties of the paste.

$$P_{\mathrm{e}} = 2 \ln \frac{D_0}{D} \left[\sigma_0 + \sqrt{2}K(2\sqrt{2})^{\mathrm{m}} \left(\frac{V}{D}\right)^{\mathrm{m}}\right] \tag{4}$$

The principle aim of this study was to determine the effect of temperature on the extrusion behavior of a polymer/ceramic paste. Binder rheology is influenced greatly by changes in temperature and this may have a large effect on the extrusion behavior The Benbow and Bridgwater equations and parameters have been used as a method for examining the variation in the extrusion behavior with temperature. A model was then developed for the extrusion behavior that incorporated the effects of temperature.

2. Experimental procedure

2.1. Materials

Taphole clay paste consists of a combination of refractory grains and a polymer binder. The polymer binder used in this study was a phenolic resin solution that contained 55% novolak resin and 45% propylene glycol.[1] The refractory component of the taphole clay matrix material consisted of a mixture of alumina (Al_2O_3), silicon carbide (SiC), coke, ferro-silicon nitride (Fe-Si_3N_4) and small amounts of other additives used to aid sintering. All the powders used had a particle size less than 150 μm. The majority of taphole clay used in industry also contains larger aggregate. Due to the scale of the experiments conducted in the present study only the finer grains were used. Further work will be performed to verify the results of this study for taphole clays containing larger aggregate.

2.2. Viscometry

A RVTCP Wells-Brookfield cone and plate viscometer was used to measure the viscosity of the polymer binder at different temperatures. The cone used was a CP-51, with a radius of 12 mm and a cone angle of 1.565°. A platinum resistance thermometer (PT1000) was mounted into the bottom of the cup so the temperature of the polymer binder at the time of measurement was known (±0.5°C). The temperature was maintained using a thermostated water bath. Recirculating water was pumped through the viscometer's cone and plate maintaining the temperature of the equipment. The viscometer had a shear rate range of 1.92 to 384 s^{-1}.

2.3. Paste preparation

The taphole clay paste samples were produced by mixing the binder and the powder in a planetary mixer for several minutes until the binder had completely been absorbed into the powder and the mixture appeared to be dry. The paste was then extruded through a mincer three times to attain well mixed material as recommended by several authors [11, 12]. The mincer was a single screw extruder with a barrel diameter of 65 mm and a die with multiple orifices of 4 mm diameter. After the material had been mixed it was stored at 30°C for 24 h.

2.4. Extrusion operation

The extrusion pressure equipment was based on the apparatus developed by Benbow and Bridgwater [1]. The equipment consisted of a barrel with an internal diameter of 25 mm with a die of 3 mm diameter. The lengths of the dies were 49, 25, and 4 mm (corresponding to L/D ratios of 16.33, 8.33 and 1.67, respectively). A ram with a 25 mm teflon washer on the end, was attached to a 10 kN load cell in an Instron tensile testing machine. The temperature was maintained by enclosing the extrusion rig in a heat box. The samples were tested at 30, 40, 50, and 60°C. The taphole clay material was placed in the barrel of the extrusion rig and

[1]Manufactured by Huntsman Chemical Company Australia Pvt. Ltd.

the ram placed into it on top of the material. The Instron controlled the speed of the ram as it descended into the barrel and compressed the taphole clay material extruding it out through the die. The taphole clay mixture was extruded at 4 different ram rates. The ram rates used were: 10, 3, 1, and 0.1 mm/min. These figures correspond to extrudate speeds of: 11.57, 3.47, 1.157 and 0.1157 mm/s respectively. This procedure was repeated for each of the different die lengths. At each temperature two sets of extrusion experiments were performed. The extrusion parameters were determined using the method established by Benbow and Bridgwater [1].

3. Results and discussion

3.1. The effect of temperature on extrusion

The Benbow and Bridgwater extrusion analysis was performed on polymer/ceramic refractory pastes at four different temperatures. An example of the extrusion pressure variation with temperature is given in Fig. 2. The extrusion pressure was found to decrease as the extrusion temperature increased.

The Benbow and Bridgwater linear (Equation 1) and non-linear (Equation 2) parameters were calculated from the extrusion data at each of the four different temperatures. An example is given in Fig. 3 of the raw extrusion pressure data and the linear and non-linear models calculated from the data. Although the linear and the non-linear models had slight differences, both models appeared to replicate the results well. For ease of analysis, the linear Benbow and Bridgwater model was employed in the remainder of this study.

At each extrusion temperature examined, the Benbow and Bridgwater parameters were calculated. Fig. 4 shows the effect of temperature on each of the averaged Benbow and Bridgwater parameters. Temperature appeared to have a significant effect on three of the four Benbow and Bridgwater parameters. The values for the initial wall stress (τ_0), the wall velocity factor (β), and the yield stress at zero velocity (σ_0) all decreased with temperature. The values for the yield stress velocity factor (α) did not exhibit a trend and appeared to be independent of the effects of temperature over the range studied. The errors associated with the Benbow and Bridgwater parameters also increased with a decrease in temperature. At lower temperatures, the paste is less workable and requires a greater extrusion pressure. It is possible that as the paste becomes less workable, the flow behaviour in the die will change resulting in larger amounts of friction both within the paste and along the die wall. This change in flow behaviour may increase the variability of the extrusion results and produce the larger error observed.

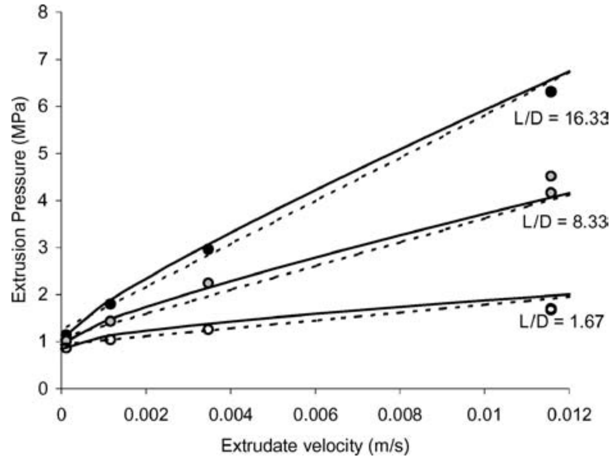

Figure 3 Polymer/ceramic refractory paste extrusion pressures plotted against the extrusion velocity at different die diameter to length (L/D) ratios. The modelled linear (Equation 1, dashed line) and non-linear (Equation 2, solid line) Benbow and Bridgwater extrusion model calculated from the data is also shown.

From these extrusion pressure results, it can be seen that care is required when handling taphole clay. If the temperature of extrusion is too low, the extrusion pressure required will be very high and small temperature variations can cause significant changes to the extrusion pressure behaviour.

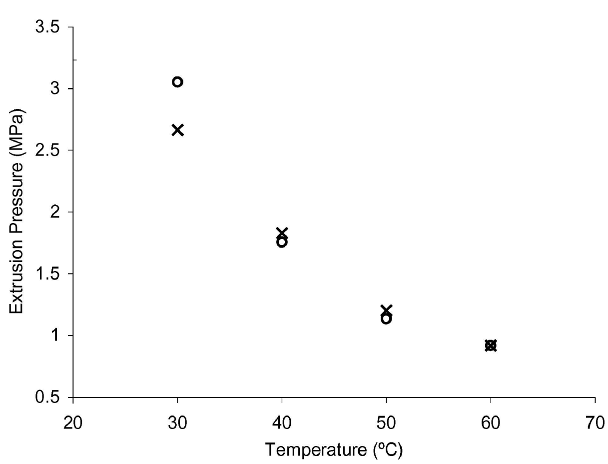

Figure 2 The extrusion pressure of two samples (○ and ×) of polymer/ceramic refractory paste, at an extrudate velocity of 1.157 mm/s and a die diameter to length ratio (L/D) of 8.33, as a function of temperature.

3.2. Influence of the binder's viscosity on extrusion

Benbow *et al.* [7] found that the extrusion of pastes was highly dependent upon the rheology of the binder. The aim of this section of the study was to quantify how the viscosity of the binder affected the extrusion behaviour of the paste. This should provide explanations for the variations observed in the extrusion pressure as the temperature was varied.

The viscosity of the binder was assessed over a temperature range of 20 to 60°C (Fig. 5). It was found that the viscosity of the binder decreased as the temperature increased. An Arrhenius model was used to describe the viscosity temperature relationship. The general form of the Arrhenius relationship used in the viscosity analysis was: $\eta = Ae^{B/RT}$ where η is viscosity and A and B are constants [13].

To examine the effect of the binder's viscosity on the extrusion pressure for the polymer/ceramic paste the viscosity of the polymer binder was related to the extrusion parameters. Fig. 6 shows the relationships between the viscosity of the binder and the Benbow and

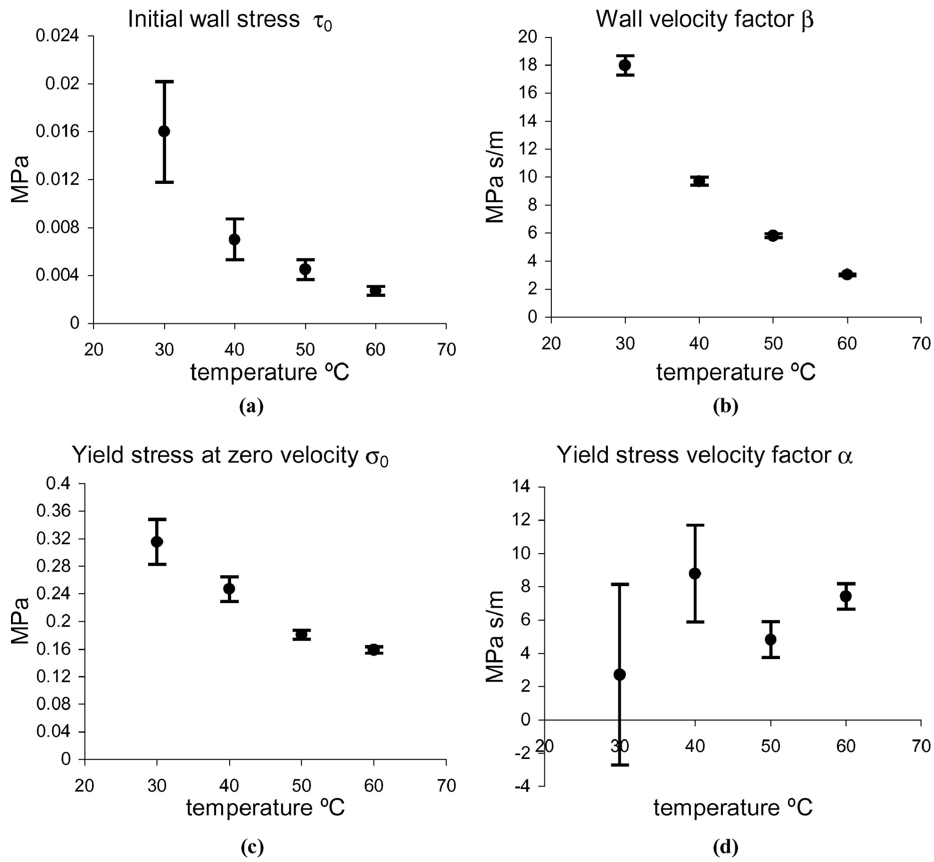

Figure 4 The Benbow-Bridgwater parameters at different temperatures: (a) Initial wall stress τ_0, (b) Wall velocity factor β, (c) Yield stress at zero velocity σ_0, and (d) Yield stress velocity factor α.

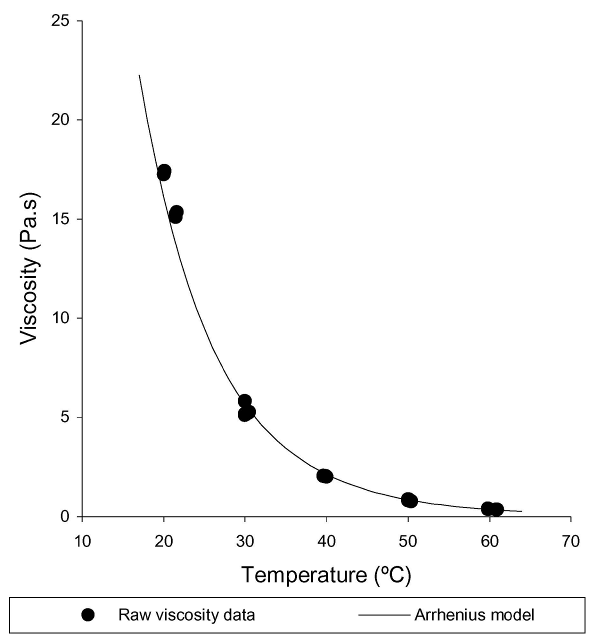

Figure 5 Change in viscosity with temperature for a polymer binder (novolak resin propylene glycol solution) including the Arrhenius model resolved from the data.

Bridgwater extrusion pressure parameters of the polymer/ceramic refractory paste. Each point on the graphs represents a different measurement temperature. The points with a higher magnitude represent the measurements taken at the lower temperature and the lower points are those taken at higher temperatures.

The viscosity of the binder appears to have an effect on three of the four Benbow and Bridgwater extrusion parameters. The values for τ_0, β, and σ_0 appear to be dependent on the behaviour of the viscosity of the binder. The values for α do not appear to be strongly influenced by the viscosity of the binder.

The τ_0 of the paste was found to have a linear dependence on the viscosity of the binder (Fig. 6a). The τ_0 is influenced by the behaviour of the binder at the die walls. If the flow in the die is purely plug flow, then shearing should occur in a thin layer of binder at the walls. If the binder used does not have a yield stress, the value for τ_0 will be close to zero. Novolak resins are a Newtonian fluid and thus have no yield stress. However, the initial wall stress increases with an increase in the viscosity of the binder. This suggests that the shear does not occur solely in a binder layer at the die wall. A similar observation has been made by Benbow *et al.* [7] who also found the flow in the die was not entirely dominated by plug flow. In the case of the polymer/ceramic paste used in this study, the viscosity of the binder may have affected the formation of the liquid binder layer at the die wall. As the viscosity of the binder increases (with a decrease in temperature) the formation of the liquid layer at the wall may have been more arduous, which may account for the increase in τ_0.

The relationship between β and the binder viscosity appears also to be reasonably linear up to 50°C (Fig. 6b), but Benbow and Bridgwater [1] state that β should be directly proportional to the viscosity of the binder assuming minimal yield stress. Therefore,

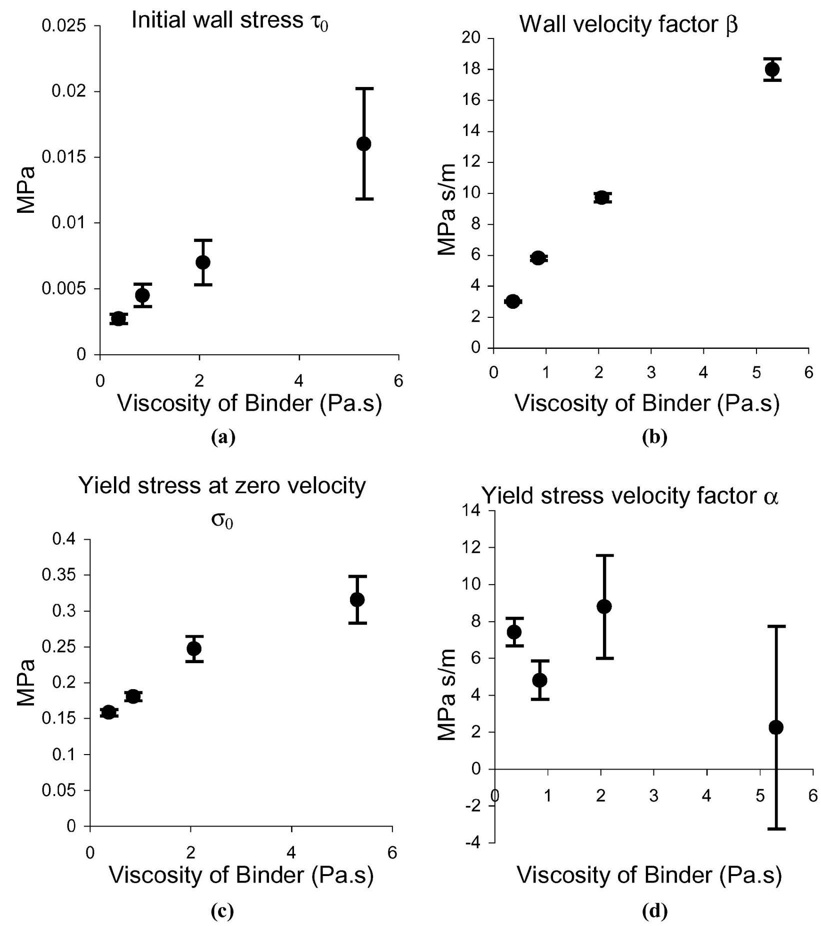

Figure 6 The averaged Benbow and Bridgwater parameters versus the viscosity of the binder: (a) Initial wall stress τ_0, (b) Wall velocity factor β, (c) Yield stress at zero velocity σ_0, and (d) Yield stress velocity factor α.

this relationship will only hold if τ_0 is much lower than βV. The range of βV values in these experiments varies from 208 kPa at 30°C to 0.35 kPa at 60°C. At 30°C the values for βV are greater than for the values of τ_0 (12 to 20 kPa) but at 60°C the values for τ_0 (26 to 28 kPa) are greater than βV. As τ_0 is not lower than βV, β will not be directly proportional to the viscosity of the binder, which may account for the lower than expected value for β at the higher temperatures.

The flow of the material into the die, which generates the yield stresses, occurs by shearing. The liquid binder between the particles of the material absorbs the shearing stresses and has a large influence on the rheology of the paste. If the viscosity of the binder increases the shear stress required to generate the same shear flow in the paste will increase. Therefore, the yield stress will increase as the binder viscosity increases. The yield stress, σ_0, does exhibit a strong relationship with binder viscosity (Fig. 6c). This relationship is not precisely linear and other forces may be associated with the paste behaviour. For example, surface tension of the taphole clay binder may also have an effect on σ_0. The surface tension and the resultant capillary forces present within the taphole clay structure could affect the strength of the material and as surface tension is dependent on temperature this may effect the relationship between σ_0 and temperature [13]. However, α appears to be independent of the viscosity of the binder. It is not clear at this stage why α does not appear to be dependent on temperature or the viscosity of the binder. Zheng *et al.* [9] related α to the shear rate factor, K, in the Herschel–Bulkley equation. Therefore, the values for α should have a relationship with the viscosity of the binder and the temperature of extrusion as both of these factors have a substantial effect on the behaviour of the paste. The value for α could also be influenced by liquid phase migration [14]. Liquid binder movement away from the die entry region may occur. Although no liquid migration was detected during the extrusions, factors such as this may account for the variability observed in α. The most probable explanation is that the large errors associated with the yield stress velocity factors have obscured any relationship.

3.3. Extrusion model accounting for temperature

Three of the four Benbow-Bridgwater parameters appear to have an approximately linear relationships with the viscosity of the binder. The viscosity of the binder was found to exhibit an Arrhenius relationship (Fig. 5). Therefore, it is proposed that the Benbow-Bridgwater parameters will also exhibit an Arrhenius relationship ($\eta = Ae^{\mathrm{B/RT}}$) [13]. When used to depict the viscosity of a liquid the constant B is known as ΔE_a, the flow activation energy and A, is a constant that incorporates the molecular weight and structural factors. From the general form of the Arrhenius relationship, the constants

TABLE I The constants A and B from the Arrhenius relationships of τ_0, β, and σ_0

Benbow-Bridgwater parameter	B (kJ)	A (units are the same as the parameter's)
τ_0 (MPa)	49.2	6.1×10^{-8}
β (MPa s/m)	48.4	6.7×10^{-11}
σ_0 (MPa)	20.0	1.1×10^{-4}

A and B can be calculated for the Benbow-Bridgwater parameters τ_0, β, and σ_0. These values are given in Table I.

The value for B is an activation energy for each of the parameters presumably related to the viscosity. The B values for τ_0 and β were close possibly because τ_0 and β are related to the flow of the paste in the die and thus their activation energy could be related to the flow activation energy for liquid viscosity. The Arrhenius constants associated with σ_0 were different from the other constants. σ_0 did not appear to have an entirely linear relationship with viscosity and seems to be somewhat dependent on other factors. The values for A incorporate structural factors associated with the viscosity as well as other compositional factors particular to the parameter. The specific factors that affect these constants will not be discussed, as further work is required. Understanding these Arrhenius constants would provide further insight into the effect of temperature and binder rheology on extrusion.

If the constants A and B for each of the three parameters are incorporated into the Benbow-Bridgwater equation, the extrusion pressure could be determined at different temperatures (Equation 5). This temperature modified Benbow-Bridgwater equation yields a value for the extrusion pressure accounting for temperature, P_T. The constants A and B are defined by the subscripts: σ_0, τ_0 and β. The values for α were averaged and the resultant value described as

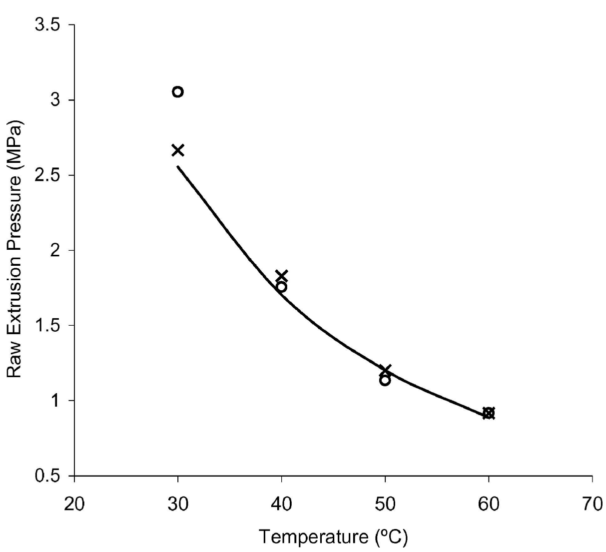

Figure 7 The extrusion pressure of two samples (○ and ×) of polymer/ceramic refractory paste, at an extrudate velocity of 1.157 mm/s and a die diameter to length ratio (L/D) of 8.33, as a function of temperature. Included is the extrusion pressure data (P_T) calculated from the modified Benbow-Bridgwater equation.

α_{av}. In Fig. 7 an example is given of how the modified Benbow-Bridgwater equation fits the experimental data. The modified Benbow-Bridgwater equation appears to model the data well. There is a small amount of deviation from the data at 30°C but this may well be due to the larger errors observed at this temperature.

$$P_T = \left(A_{\sigma_0} e^{B_{\sigma_0}/RT} + \alpha_{av} V\right) \ln(D_0/D) + 4\left(A_{\tau_0} e^{B_{\tau_0}/RT} + A_\beta e^{B_\beta/RT} V\right)(L/D) \quad (5)$$

It can be argued that the raw extrusion pressure data would fit an Arrhenius relationship. However, the extrusion pressures at each extrudate velocity (V) and die length to diameter ratio (L/D) would yield a different value for the Arrhenius constants. Thus, the model would be based on the experimental conditions and not a material property. The Benbow-Bridgwater parameters are constant within the range of conditions used. As the Arrhenius plots were devised for the three parameters, they should provide an estimate of the extrusion pressures at different temperatures and under different experimental conditions within the ranges selected. The temperature modified Benbow–Bridgwater equation can compare the extrusion pressure of the material at different extrudate velocities and die length to diameter ratios.

The use of the temperature modified Benbow and Bridgwater equation could help in the handling and use of taphole clay materials. Using this equation, it may be possible to have more control over taphole clay properties by manipulating the extrusion pressure. The Benbow and Bridgwater parameters would be different depending on the specific composition used but once they were established for a particular taphole clay the temperature could be controlled to establish the desired extrusion pressure.

4. Conclusions

The effect of temperature variation on the extrusion behavior of a polymer/ceramic refractory paste was found to be significant. The extrusion pressure decreased considerably when the extrusion temperature was increased. The Benbow and Bridgwater parameters of initial wall stress (τ_0), wall velocity factor (β), and yield stress at zero velocity (σ_0) were also found to decrease with temperature. However, the yield stress velocity factor (α), as found to bear no strong relationship with temperature.

The viscosity of the binder was also found to decrease as the temperature increased. The viscosity appears to have a large influence on three of the four Benbow and Bridgwater extrusion parameters. A correlation was established between three of the Benbow and Bridgwater parameters (τ_0, β, and σ_0) and the viscosity of the binder. The variation of the viscosity can explain much of the variation seen in the extrusion pressure as the temperature is varied.

Utilising an Arrhenius model for three of the Benbow and Bridgwater parameters and an averaged value for α, a modified Benbow-Bridgwater equation was created.

This model takes into account the effect of temperature on the extrusion pressures of the polymer/ceramic refractory paste. These findings should be useful for controlling the extrusion of taphole clay into an iron making blast furnace. Further work is required to fully understand the factors that influence the Arrhenius constants for each of the Benbow-Bridgwater parameters.

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