Review

Slag Behavior in Gasifiers. Part II: Constitutive Modeling of Slag

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Abstract: The viscosity of slag and the thermal conductivity of ash deposits are among two of the most important constitutive parameters that need to be studied. The accurate formulation or representations of the (transport) properties of coal present a special challenge of modeling efforts in computational fluid dynamics applications. Studies have indicated that slag viscosity must be within a certain range of temperatures for tapping and the membrane wall to be accessible, for example, between 1,300 °C and 1,500 °C, the viscosity is approximately 25 Pa·s. As the operating temperature decreases, the slag cools and solid crystals begin to form. Since slag behaves as a non-linear fluid, we discuss the constitutive modeling of slag and the important parameters that must be studied. We propose a new constitutive model, where the stress tensor not only has a yield stress part, but it also has a viscous part with a shear rate dependency of the viscosity, along with temperature and concentration dependency, while allowing for the possibility of the normal stress effects. In Part I, we reviewed, identify and discuss the key coal ash properties and the operating conditions impacting slag behavior.

1. Introduction

Deposition of ash in fluidized-bed combustion is primarily caused by the transfer of molten mineral matter from the burning char onto the bed surface. Two possible mechanisms have been proposed for this unwanted phenomenon: (1) partial melting or reactive liquid sintering, and (2) viscous flow sintering [1]. The first situation occurs with partial melt at 500–700 °C, which is normally lower than the standard operating temperatures of many fluidized beds. The second mechanism occurs at temperatures about or higher than 1,000 °C, creating a highly viscous and non-linear fluid. At such high temperatures, the standard methods of measuring viscosity do not always work. Heat transfer at the walls of a combustor depends on many parameters including ash deposition. This depends on the processes or parameters controlling the impact efficiency and the sticking efficiency [2,3]. The main problems with ash deposition are reduced heat transfer in the boiler and corrosion of the tubes. Common ways of dealing with these issues are soot blowing and wall blowing on a routine basis; however, unexpected or uncontrolled depositions can also complicate the situation and there are always locations inaccessible to the use of such techniques. Wang and Harb [4] list eight important concepts which should be addressed in any formation of ash deposits modeling: (1) understating the process of ash formation; (2) understanding the fluid dynamics and the equations governing the particle transport; (3) the process of particle impacts and sticking to the surfaces; (4) the location of deposit growth in the combustion chamber, (5) deposit properties, (6) heat transfer mechanisms through the deposit layers, (7) the effect of deposition on temperatures and heat fluxes, *etc.*, and (8) the structure of deposit and how this affects the flow patterns in the combustion facility. Erickson *et al.* [5] proposed three distinct layers, which include: (1) an initial layer deposit formed by small ash particles, (2) a bulk layer formed from the partially molten ash and the non-deformable particles captured by the deposit surface, and (3) a slag layer flowing as a viscous fluid.

One of the main reasons for using an entrained-flow gasifier is that the highest temperature can be achieved in the entrained-flow slagging process [6]. Next to the viscosity of ash or slag, thermal conductivity is the most important physical /material parameter. The ash deposits are porous and they can be approximated as packed beds. For a detailed analysis and a discussion of the relevant issues to heat transfer in ash deposits, we refer the reader to the review article by Zbogar *et al.* [7]. Jak *et al.* [8] mention that the major components of coal slags produced in combustion or gasification processes are based on FeO-Fe_2O_3-CaO-SiO_2-Al_2O_3 chemical composition (Interestingly, the chemistry of many metallurgical smelting operations also depend on a similar chemical compositions but with seven components, instead of five, namely, PbO-ZnO-FeO-Fe_2O_3-CaO-SiO_2-Al_2O_3).. In their study, they used a modified quasi-chemical model for the molten slag phase, and the thermodynamic modeling was based on the FACT computer system [9]. As Jak *et al.* [8] mention: "The slag composition and operating temperature should be such that a small temperature decrease in the reactor or a small variation in slag chemistry does not lead to a large increase in the fraction of solids in the slag." This is an issue related to the control of the slag layer, where it is preferable for the slag to behave like a fluid so that it can be tapped from the reactor [10].

A common definition of "slagging" is the deposition of ash in the radiative section of a boiler (whereas "fouling" refers to the deposition of ash in the convective-pass region) [5]. Slag and ash also occur in ignite-fired power plants whose main characteristics are a high water and ash content [11].

Vorres *et al.* [12] observed that in regions where there is a large amount of iron present in the coal ash, especially in the eastern parts of the United States, in the more oxidizing environment of a boiler, coal slags behave more like a highly polymerized fluid than in the less oxidizing environments such as the slagging gasifier or cyclone combustor [13]. As Jak *et al.* [14] observed, at a typical section of slag deposit on the walls of a reactor, the temperature at the water-cooled wall of a gasifier can be taken to be ~450 °C, while the temperature at the slag surface is ~1450 °C. Such a sharp gradient causes various types of responses including the creation of different sub-layers. Studies have indicated that slag viscosity must be within a certain range of temperatures for tapping and for the membrane wall to be accessible, for example, between 1,300 °C and 1,500 °C, the viscosity is approximately 25 Pa·s [15].

In recent years, one of the approaches to improve the production efficiency of blast furnaces has been to include low slag volume by using high pulverized coal injection (PCI) operation. In many cases, as Kang *et al.* [16] observed, the fluidity of blast furnace slag is controlled by changing the slag chemistry. Kang *et al.* [16] indicate that not only is the viscosity of slag important in these operations, but also coke/slag interactions, which could significantly impact the liquid permeability of the blast furnace. There is a great deal of similarity in the processes involving steel production and those of slag in coal gasification or combustion processes. Important issues in thermal processing of steel ingots include thermal stress modeling and panel cracking [17–19].

The world demand for building supplies requires large amounts of raw materials. A new emerging area is the use of slag from the industrial streams, such as blast furnaces slag, in building materials [20]. There have also been studies on freeze-thaw cycle on alkali-activated slag concrete [21]. Slag cement and other viscosity modifying admixtures (VMAs) have been used in recent years in self-consolidating concrete (SCC) with some success [22]. As fossil fuel use increases, the amount of waste materials and the environmental issues dealing with their disposal also increase. One of the promising approaches is the development of coal/waste co-firing technology with fuels such as biomass. Biomass constitutes an estimated 14% of the world energy use, which makes it the fourth largest energy source [23]. Biomass can comprise wood residues, agricultural residues (crops, foods, animals), municipal solid waste, *etc.* [24]. Additionally, energy crops, including short-rotation woody crops and herbaceous crops such as tall switch grass, are predicted to become the largest source of biomass in the future. In general, biomass fuels are converted to energy via thermal, biological, and physical processes. Bridgwater *et al.* [25] and Bridgwater [26] indicate that the three primary thermal processes for converting biomass to useful energy are combustion, gasification, and pyrolysis. Coal can be used as the primary fuel for high temperature environments such as the open-cycle Magneto-hydrodynamics MHD generators where coal particles are burnt in the combustion chamber with temperatures and pressures in the order of 3,000 K and 10 atm, respectively. Under these high-temperature and high-pressure conditions, the dynamics of coal particles change significantly. As mentioned by Sondreal *et al.* [27] high temperatures are needed for most advanced combustion technologies, including those using co-firing biomass with fossil fuels, to improve the thermodynamic efficiencies, which in turn raises problems associated with high temperature such as corrosion and deposition by coal ash and slag. Slagging combustors have been used in more recent MHD applications [28] in conjunction with an advanced gasifier system, known as the Multistaged Enthalpy Extraction Technology (MEET) [29]. According to these researchers, improvements in coal gasification, cleanup,

turbine generators, system integration, *etc.*, improve efficiency in integrated gasification combined cycle (IGCC) plants.

One way of improving the efficiency in IGCC processes is to use a two-stage feeding, which involves a combustion stage and a reduction stage with a gasifier. Chen *et al.* [30] developed a numerical model for a two-phase type flow, using the K-ε turbulence model for the gas and a particle dispersion model, emphasizing that the movement of particles is the primary parameter determining the local fuel-O stoichiometric ratio, which is important in controlling the overall carbon conversion. The accurate formulation or representations of the (transport) properties of coal (and biomass for co-firing cases) present a special challenge of modeling efforts in computational fluid dynamics (CFD) applications. For example, we do not possess a good knowledge of the specific heats of coals as a function of temperature at high heating rates [31]. As pointed out by Backreedy *et al.* [32], in most CFD studies related to coal combustion, the effects of gravity are assumed to be negligible. This is not a good assumption, since in many processes, especially co-firing with biomass, 10%–40% of the ash can fall into the bottom ash hopper. In recent years, many CFD codes have been developed. An important issue is the physical models which are embedded in these codes; most of these models are linear constitutive equations. Bjorkvall *et al.* [33] presented a multi-component model where the oxide activities, the determining or the driving force of the chemical reactions, was obtained based on the experimental information corresponding to the binary subsystem. Some of the carbon associated with char particles are unburnt and are transferred to the molten ash slag. Montagnaro and Salatino [34] studied the coal particles in an entrained gasifier in the slagging regime. They developed a simple one-dimensional model of the gasifier by suggesting that the gasifier can be divided into three components, namely, a lean-dispersed phase, a wall ash layer, and a dense-dispersed phase. Ni *et al.* [6] used an Eulerian-Lagrangian approach to study the flow of the gas and particle phases.

Among the computational codes one can name the particle-size and composition distribution (PSCD) of the ash produced in combustion and other simplified transport models. However, as Ma *et al.* [35] observed, there does not seem to be a comprehensive and integrative approach in the codes to predict the deposit formation and growth in specific areas and its impact on the total heat transfer in the boiler. Ma *et al.* [35] present their results based on a computer code named AshPro[SM], which can obtain information about slagging and fouling at specific localized points. One of the latest studies by Koric and Thomas [36] considers two different elastic visco-plastic models for the behavior of steel solidification. To do their study, they used a model developed by Anand [37] in the commercially available code ANSYS and the model by Kozlowski *et al.* [38] using the commercially available ABAQUS code. In both classes of models the strain rates are given by experimentally obtained/fitted correlations that are functions of temperature, stresses, chemical composition, *etc.* To develop an accurate heat transfer model in any type of coal combustion or gasification process, the heat transfer and to some extent the rheological properties of ash and slag, especially in high-temperature environments need to be understood and modeled properly. It has been recognized that the viscosity of slag and the thermal conductivity of ash deposits are two of the most important constitutive parameters that must be studied. As Rezaei *et al.* [39] state, the latter depends on the porosity, chemical composition, temperature of the deposit, *etc.* They observed that the thermal conductivity of ash increases with increasing temperature, but decreases with increasing porosity. Noticeably, the thermal

conductivity of slags was found to be higher than that of the particulate structure in the porosity range 0.2–0.8.

In this paper, we first provide a brief review of the various approaches taken by different researchers in formulating or obtaining a slag viscosity model. In general, these models are based on experiments. Since slag behaves as a non-linear fluid, we discuss the constitutive modeling of slag and the important parameters that must be studied. Based on this brief review, a new constitutive model is proposed, where the stress tensor is not only represented by a yield stress part, but it also has a viscous part which is capable of demonstrating shear rate dependency of the viscosity, along with temperature and concentration dependency, while allowing for the possibility of the normal stress effects.

In the next section of this paper, we present the basic governing equations for the flow of slag if it is considered as a non-homogeneous and non-linear single component material. Massoudi and Wang [40] discuss cases where slag may be modeled as a part of a multi-component or a two-component system (such as gasification) where generally a two-fluid (Eulerian-Eulerian) approach is used, or as a part of a (dilute) multi-component (Lagrangian-Eulerian) system.

2. Governing Equations of Motion and Heat Transfer

If slag is treated as a single component (phase) material, then, in the absence of any electro-magnetic effects, the governing equations of motion are the conservation of mass, linear momentum, convection-diffusion, and energy equations [41]:

Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \mathrm{div}\,(\rho \mathbf{u}) = 0 \tag{2.1}$$

where ρ is the density of the fluid, $\partial/\partial t$ is the partial derivative with respect to time, and $\mathbf{u}$ is the velocity vector. For an isochoric motion, we have $\mathrm{div}\,\mathbf{u} = 0$.

Conservation of linear momentum:

$$\rho \frac{d\mathbf{u}}{dt} = \mathrm{div}\mathbf{T} + \rho \mathbf{b} \tag{2.2}$$

where $\mathbf{b}$ is the body force vector, $\mathbf{T}$ is the Cauchy stress tensor, and d/dt is the total time derivative, given by $\frac{d(.)}{dt} = \frac{\partial(.)}{\partial t} + [\mathrm{grad}(.)]\mathbf{u}$. The balance of moment of momentum reveals that, in the absence of couple stresses, the stress tensor is symmetric.

Conservation of Concentration:

$$\frac{\partial c}{\partial t} + \mathrm{div}\,(c\mathbf{u}) = f \tag{2.3}$$

where c is the concentration and f is a constitutive parameter. This equation is also known as the convection-reaction-diffusion equation.

Conservation of Energy:

$$\rho \frac{d\varepsilon}{dt} = \mathbf{T} \cdot \mathbf{L} - \mathrm{div}\mathbf{q} + \rho r \tag{2.4}$$

where ε is the specific internal energy, **L** is the gradient of velocity, **q** is the heat flux vector, and r is the radiant heating. Thermodynamical considerations require the application of the second law of thermodynamics or the entropy inequality. The local form of the entropy inequality is given by (see Liu [42], p. 130):

$$\rho\dot{\eta} + \text{div}\,\boldsymbol{\varphi} - \rho s \geq 0 \tag{2.5}$$

where $\eta(\mathbf{x}, t)$ is the specific entropy density, $\varphi(\mathbf{x}, t)$ is the entropy flux, and s is the entropy supply density due to external sources, and the dot denotes the material time derivative. If it is assumed that $\boldsymbol{\varphi} = \dfrac{1}{\theta}\mathbf{q}$, and $s = \dfrac{1}{\theta}r$, where θ is the absolute temperature, then Equation (2.5) reduces to the Clausius-Duhem inequality:

$$\rho\dot{\eta} + \text{div}\frac{\mathbf{q}}{\theta} - \rho\frac{r}{\theta} \geq 0 \tag{2.6}$$

Even though we do not consider the effects of the Clausius-Duhem inequality in our problem, for a complete thermo-mechanical study of this problem, the Second Law of Thermodynamics must be considered [42–45]. To achieve "closure" for these equations, in general, we must provide constitutive relations for **T**, **q**, f, ε and r. In certain applications, some of these effects can be ignored. Nevertheless, the constitutive modeling of **T** and **q** remain a challenge in the problems or industrial applications related to thermofluid mechanics. In the next section, we discuss the various approaches taken by different researchers in formulating or obtaining a slag viscosity model. In general, these models are based on experiments.

3. The Importance of Slag layer Viscosity in Gasification and Combustion Processes

3.1. Viscosity of Slags

In one of the earliest studies, Bills [46] reported that the addition of calcium fluoride leads to a lowering of the slag viscosity. In the blast furnace slag system, the impact of MgO on the viscosity of slag is of interest. Kim *et al.* [47] used the rotating spindle connected to a Brookfield digital viscometer to measure the viscosity of slag containing MgO at high concentrations of Al_2O_3, while Xu *et al.* [48] used an RTW-08 type testing instrument to measure the viscosity of $CaO-Al_2O_3-MgO$ slag systems. It is interesting that fluxing compounds such as calcium oxide, which are added to coals primarily to reduce the slag viscosity, play a similar role as polymeric additives, which are added to many fluids to reduce the drag.

As the operating temperature decreases, the slag cools, and solid crystals begin to form. In such cases, the slag should be regarded as a non-Newtonian suspension, consisting of liquid silicate and crystals [49]. In such cases, a better understanding of the rheological properties of the slag, such as yield stress and shear-thinning, are critical in determining the optimum operating conditions. Groen *et al.* [50] observed that, in slags where titanium-rich feeds are used, the melting point is lowered up to 27.5%, and, where calcium-rich feeds are used, there is an increase in the glass fluidity for CaO contents up to 30%, regardless of the amount of titanium present in the feed. They noticed that at the critical viscosity temperature, T_{cv}, the slag changes from a homogeneous fluid to a mixture

composed of fluid and a crystallizing phase (solid), where there is an increase in the (apparent) viscosity due to the presence of the crystals or the change in the melt composition. Kong *et al.* [51] observed that adding pulverized limestone with the effective ingredient of CaO improves slag flow properties. They also noticed that, at the temperatures below the temperature of critical viscosity, referred to in their analysis as T_{cv}, the slag behavior is non-Newtonian. Stanmore and Budd [52] point out that ashes formed in the 0.1–10 MPa-s range, which are generally at temperatures above 1000 °C (assumed normally to behave as Newtonian fluids), are in fact very likely to be two- or multi-phase mixtures. They indicated that both yield stress and yield viscosity (Bingham viscosity) depend on temperature. They used the squeeze film rheometer to measure the viscosity. For a detailed analysis of using the programmable Brookfield LVDV-II+ viscometer and how it can be used to measure the viscosities of slag with fluxes [53]. For using the rotating crucible viscometer to measure the viscosity of blast furnace type slags, we refer the reader to Saito *et al.* [54]. Pandey *et al.* [55] presented a novel technique, whereby they attempted to measure the properties of mould powder slags, such as viscosity, liquidus temperature, *etc.*, using ultrasonics.

According to Seetharaman *et al.* [56], most slags are ionic in nature. Their viscosities are very sensitive to the size of the ions and the electrostatic interactions, and, as more and more basic oxides are added to pure silica, the silicate network breaks down, and viscosity begins to decrease gradually. In addition to discussing the traditional methods of measuring slag viscosity, Seetharaman *et al.* [56] mention two other related concepts: the surface dilatational viscosity and the two-phase viscosity. They suggest that surface dilatational viscosity, although very difficult to measure at high temperatures, is an important quantity to be considered especially when foaming, coalescing bubbles, dispersion of droplets or solid particles, *etc.* For the two-phase viscosity, they suggest using the two well-known equations for viscosity based on the works of Einstein [57] and the later contribution by Taylor [58] and Batchleor [59].

In general, the feedstock for a given gasification process may include coal, heavy oil, coke, and wastes such as sewage sludge, biomass or even scrap tire. The gasification of petroleum coke is receiving more attention because of its heating value and low cost, while pressing special challenges due to its composition: vanadium, nickel, and iron. Park and Oh [60] studied the viscosity of Korean anthracite slag, which contains a large portion of vanadium trioxide (V_2O_3). They observed that, in order to keep the slag flowing, the temperature had to be kept above 1,670 °C, which is 270 °C above the typical operating temperature for slurry-feed gasifiers. Based on their experimental results, they suggested two optimum ranges for gasification, namely glassy slag and crystalline slag.

To a certain extent, magnesia raises the viscosity of slags while increasing the liquidus temperature. However, as Ducret and Rankin [61] observed, above a certain concentration, MgO increases the viscosity. They also refer to a study performed by Broadbent *et al.* [62], in which 13 reputable laboratories measured the viscosity of the same synthetic slag and obtained varied results around the mean by as much as 50%. As pointed out by Sridhar [63], slags and fluxes are commonly used in many of the iron and steel or copper making and refining industries, as well as aluminum melting. In these applications, slags provide a protection layer for the molten metal surface from the atmosphere, while absorbing the impurities during the casting and creating some lubrication between the mold and metal strand, *etc.* The most important parameter in all these cases is the slag viscosity. Sridhar [63] provides an excellent summary of a few important models for the viscosity of slags.

Patterson and Hurst [64] presented the date for slag viscosity as a function of temperature for different kinds of Australian coal. When necessary they used limestone to lower the liquidus temperature and slag viscosity for optimum operation and slag tapping. Tonmukayakul and Nguyen [1] state that traditional methods for viscosity measurements and instrumentation might be satisfactory for coal ash slags obtained from bituminous (black) coal or those with high silica content but inaccurate for the cases with lower temperatures, where the coal may be partially molten and generally behaves as a non-Newtonian fluid. To overcome this problem, they suggested using a cone and plate rheometer, in which a volume of molten ash contained between a thin gap and a plate at a small cone angle is sheared. Although they do not provide any equations, other than to state that an Arrhenius-type equation satisfactorily represents the effects of temperature for both ash samples, this study is a valuable example of how careful measurements can provide a good deal of information for modeling purposes. For example, they observed that between 1,150 °C and 1,300 °C, the data of shear stress *versus* shear rate for melt as a function of temperature indicate that the oxide melt behaves as a Newtonian fluid; however, in the temperature ranges from 850 °C to 1,200 °C, coal ash was shown to have a non-linear response, thus exhibiting non-Newtonian characteristics. Specifically, and more importantly, they mention that this ash sample (the Loy Yang coal) should be modeled as viscoplastic shear-thinning fluid with a yield stress. They conclude that the presence of a high yield stress for the slag, in the range of operating temperatures, confirm previous findings [1] that a high alkali sulphate ash is more likely to agglomerate in fluidized-bed combustion than a silica rich coal. Song *et al.* [65] devised a high-temperature rheometer to study the rheological characteristics of slag, specifically the thixotropy and yield stress at different temperatures ranging from 500 °C to 1,550 °C. Although they did not provide any equations, their results presented in graphical forms indicate that the slags behave as a thixotropic shear-thinning non-Newtonian fluid with a yield stress. Measuring yield stress is very difficult, even under normal conditions, let alone under such high temperatures. Like other researchers, Song *et al.* [65] extrapolated the straight-line section of the data in the shear-rate *vs.* shear-stress curve to obtain the value of the yield stress. They also observed that the shear-thinning became more distinct as the temperature decreased. In the next sub-section we will look at some of the most well-known viscosity models for slags.

3.2. A Brief Review of Various Viscosity Models

Watt and Fereday [66] presented one of the earliest and most comprehensive studies of the measurement of viscosity of slags using British coals and the rotating cylinder-type viscometer. Melted ash was poured into a crucible at a temperature between 1,700 °C–1,800 °C and maintained at this temperature until the value of obtained viscosity had remained constant for an hour. Using an Arrhenius type equation, they related viscosities of slags for the entire temperature range to their compositions expressed in terms of the percent by weight of SiO_2, Al_2O_3, MgO, CaO, and iron oxides, where:

$$\eta = A \exp\left(\frac{E}{RT}\right) \tag{3.1}$$

was changed into:

$$\log \eta \,(\text{in poise}) = \frac{10^7\,m}{(T-150)^2} + c \tag{3.2}$$

where m and c are given in terms of compositions and T is the temperature in degrees C, where:

$$m = 0.0083\ SiO_2 + 0.00601\ Al_2O_3 - 0.109$$

$$c = 0.0415\ SiO_2 + 0.0192\ Al_2O_3 + 0.0276\ \text{Equiv}\ Fe_2O_3 + 0.0160\ CaO - 3.92 \tag{3.3}$$

$$SiO_2 + Al_2O_3 + \text{Equiv}\ Fe_2O_3 + CaO + MgO = 100\ (wt\%)$$

They also compared their results with the so-called S^2 formula (Hoy *et al.* [67]), in which viscosity is given by the following equation:

$$\log \eta = 4.468 \left(\frac{S}{100}\right)^2 + 1.265\left(\frac{10^4}{T}\right) - 7.44 \tag{3.4}$$

where S is the silica ratio and T is the temperature given in degrees K. It was shown that the new correlation provides better comparison with the data. Kato and Minowa [68] measured the viscosity of slag composed of $CaO\text{-}SiO_2\text{-}Al_2O_3$. The effects of various other additions were also considered. They used a balanced platinum sphere viscometer and suggested the following equation:

$$\eta = KW(t_1 - t_2) \tag{3.5}$$

where K is constant related to the apparatus, W is the weight necessary to raise the sphere through the slag, t_1 is the time necessary to raise the sphere for 10 mm in the slag, and t_2 is the time required to raise the sphere in air 10mm. The temperature dependence of the viscosity was expressed by an Arrhenius-type equation, also known as the Andrade's equation:

$$\eta = A_\eta \exp\left(\frac{E_\eta}{RT}\right) \tag{3.6}$$

where A_η is a frequency factor, E_η is the activation energy, R is the gas constant, and T is the absolute temperature. It was observed that the value of E_η increases with Al_2O_3 or SiO_2 content, and that the slag is more viscous perhaps due to network formation. Overall, they found out that the viscosity coefficient and the activation energy of this molten slag increased with the increasing amount of Al_2O_3 or SiO_2 while CaO lowered these values. Furthermore, it was observed that the addition of FeO, MnO, or MgO, which are popular in steel-making, lowered the viscosity but increased the activation energy.

Perhaps the most widely used equation for the viscosity of slag is that of Urbain [69] who used basic ideas from statistical and molecular physics to relate the fluidity (the inverse of viscosity) to two probabilities related to the variable of the state and to the structure of the liquid (a measure of polymerization). He deduced that one of these probabilities, P_e, is related to the energy level of the potential. Urbain therefore used a statistical approach suggested by Weymann [70] to obtain an exponential-type equation for the viscosity. For the other probability, P_v, denoted as the 'hole' probability, Urbain suggested that it is proportional to the concentration of the 'holes' given at T via another exponential function. By combining these two functions, Urbain suggested a two-parameter expression for the viscosity:

$$\mu = AT \exp(1000B/T) \tag{3.7}$$

where A is a function of various parameters such as mass, volume of the structural unit, the energy of the well, and the partial molar entropy, and B is a function of the energy of the well and the partial molar enthalpy. Urbain showed that A and B are related through:

$$\ln A = \ln A_0 + E/(RT_c) - 1000B/T_c \tag{3.8}$$

where A_0, E and T_c are constants for a given liquid; this equation can be generalized to:

$$-\ln A = mB + n \tag{3.9}$$

where m and n are obtained from experimental data. For a group of 54 liquids, Urbain suggested the mean values of these two parameters to be:

$$m = 0.29$$
$$n = 11.57 \tag{3.10}$$

The above model has been generalized by various authors for different conditions.

Riboud and Lareecq [71] suggested that parameters A and B in the Urbain model should be polynomial functions of the composition. Kondratiev and Jak [72] used a similar argument and suggested that parameters m and n should also be functions of composition in the following manner:

$$m = m_A X_A + m_C X_C + m_F X_F + m_S X_S \tag{3.11}$$

where the m's are model parameters and the X's are the molar fractions of Al_2O_3-CaO-'FeO'-SiO_2 respectively. They obtained the optimized values of the m's by fitting the experimental values of A and B. Building on the previous modifications to the Urbain model, Kondratiev and Jak [73] suggested two different continuous functions for B for two different modifiers (FeO and CaO):

$$B = \sum_{i=0}^{3} b_i^0 X_S^i + \sum_{i=0}^{3} \sum_{j=1}^{2} \left(b_i^{Cj} \frac{X_C}{X_C + X_F} + b_i^{Fj} \frac{X_F}{X_C + X_F} \right) \alpha^j X_S^i$$
$$\alpha = \frac{X_C + X_F}{X_C + X_F + X_A} \tag{3.12 a,b}$$

where b_i^0 values are parameters for the Al_2O_3-SiO_2 system, while b_i^{Cj}, b_i^{Fj} are parameters for CaO-'FeO' system, all obtained by optimization.

Generally, the temperature of critical viscosity, T_{cv}, is defined as the temperature where the behavior of the molten ash, specifically its viscosity, changes from a Newtonian fluid to that of a non-Newtonian fluid, specifically a Bingham fluid [74,75]. At this temperature, coal ash undergoes phase transformation, which can be due to nucleation and crystal growth, phase separation, *etc.* Nowok [74] suggested that the viscosity of slag near the T_{cv} depends on the well known second order equation, in which viscosity is related to the volume faction of the solid particles:

$$\eta_{mix} = \eta_r (1 + c\phi + d\phi^2) \tag{3.13}$$

where c and d are constants related to the shape of the dispersants and solid-melt interaction, ϕ is the volume fraction, and η_r is the viscosity of the 'residual slag'. It is suggested that a sudden increase in viscosity is due to a phase transformation, which results from both a nucleation and a spinodal

decomposition. Another interesting entrained flow gasifier is the Prenflo, which operates at temperatures above ash slagging, where the molten ash accumulates at the inside walls of the gasifier, due to centrifugal forces. Between the liquid layer and the cold walls a solid slag layer is formed [76]. Reid and Cohen [77] suggested that the molten slag behaves as a Newtonian fluid above the critical temperature viscosity, T_{cv}, and as a plastic fluid below T_{cv}, while Johnson [78] assumed that molten ash behaves as a Bingham fluid over the entire range of temperatures considered. Seggiani (1998) [76] used the relative amounts of the basic and acidic constituents in the slag to predict the T_{cv} and the slag viscosity; he also indicated that specific heat and thermal conductivity are important transport quantities that need to be studied. Specifically, he suggested the following correlation for T_{cv} as a function of the acid/base ratio:

$$A/B = \frac{SiO_2 + Al_2O_3 + TiO_2}{Fe_2O_3 + CaO + MgO + Na_2O + K_2O} \tag{3.14}$$

where the slag components are given in weight percentages. Based on a linear regression, the T_{cv} was given as:

$$T_{cv} = 1385.44 + 74.1(A/B) \quad (K) \tag{3.15}$$

and:

$$\log \eta = 4.468S^2 + 1.265\left(\frac{10^4}{T}\right) - 7.44 \tag{3.16}$$

which is valid above the T_{cv}, where η is the viscosity in poise, S is the silica ratio, and T is the temperature given in degrees K.

Hurst *et al.* [79] used a Haake high-temperature rotational viscometer with molybdenum and crucibles to measure viscosity of various slags. Similar to other researchers before them, they presented in contour plots the viscosity and the T_{cv} of slags composed of 5% and 10% FeO. They used a modified Urbain model where the coefficients in the polynomial functions depend on the composition. To calculate viscosity, they suggested the following equation, based on a least squares fit of the experimental data, for the temperature range of 1,400–1,500 °C:

$$-\ln \eta = A + \frac{B}{T} \tag{3.17}$$

where A and B are given in tabular forms and their values are different for each slag. For the experimental treatment of the data, Hurst *et al.* [79] used a modified Urbain model using the Weymann equation:

$$\eta = AT\exp\left(\frac{B}{RT}\right)$$

or:

$$\ln\eta = \ln A + \ln T + \frac{B}{RT}$$
$$= a_0 + a_1 y + a_2 y^2 + a_3 x + a_4 xy + a_5 xy^2 + a_6 x^2 + a_7 x^2 y \tag{3.18}$$
$$+ a_8 x^2 y^2 + a_9 x^3 + a_{10} x^3 y + a_{11} x^3 y^2$$

where R is the gas constant and x and y are the normalized mole fractions given by:

$$x = \frac{m_s}{m_s + m_a + m_c + m_f}$$

$$y = \frac{m_c + m_f}{m_a + m_c + m_f}$$

(3.19)

This study was specifically aimed at the SiO$_2$-Al$_2$O$_3$-CaO-FeO (SACF) system at 5 and 10% wt FeO. Later, Hurst *et al.* [80] extended this study to include synthetic slags at the 15% wt FeO; they obtained similar results. Mills and Sridhar [81] also extended the Urbain model by making A and B functions of a correction factor, related to optical basicity, denoted by Λ^{corr}. They called this model the National Physical Laboratory (NPR) model and, specifically, they suggested the following correlations, which are based on experimental data:

$$\frac{\ln B}{1000} = -1.77 + \frac{2.88}{\Lambda^{corr}}$$

$$\ln A = -232.69 \left(\Lambda^{corr} \right)^2 + 357.32 \Lambda^{corr} - 144.17$$

(3.20)

Iida *et al.* [82] suggested a viscosity model where the effects of the slag through the (network) structure are taken into account by the basicity of slag. Thus:

$$\mu = \mu_0 A \exp\left(\frac{E}{Bi^*} \right)$$

(3.21)

where:

$$A = 1.745 - 1.962 \times 10^{-3} T + 7 \times 10^{-7} T^2$$

$$E = 11.11 - 3.65 \times 10^{-3} T$$

(3.22)

where A and E are parameters to be fitted from the experimental data, and μ_0 is the hypothetical viscosity of the non-networking slag expressed as a complicated exponential function, which depends on many parameters such as the molar volume at the melting temperature, the gas constant, the mole fraction, *etc.* The modified 'basicity' index Bi^* was calculated from another complicated function that depends on many parameters, especially on the mass percentage of the various components present in the slag, for example, CaO-SiO$_2$-Al$_2$O$_3$-MgO, *etc.* Reddy and Hebbar [83], based on the works of Bockris and Reddy [84] and their own earlier work [85], suggested the following equation for the viscosity of slag:

$$\eta = 4.9 \times 10^{-10} N_O^0 T^{1/2} \exp\left(\frac{E}{RT} \right)$$

(3.23)

where the N_O^0 value takes into account the depolymerization and subsequent breakdown of the silicate network structure, and E is the energy needed to break the bond, given by a polynomial function:

$$E = \alpha + \beta N_O^0 + \gamma (N_O^0)^2 + \delta (N_O^0)^3 + \varepsilon (N_O^0)^4$$

(3.24)

where $\alpha, \beta, \gamma, \varepsilon$ are functions of temperature given by experimental correlations in the polynomial form.

It is known that in IGCC slagging gasifiers, the (coal ash) slags should be 'fluid' enough to be tapped. However, in many cases, the IGCC processes operate at conditions where there are still some

solid particles in the liquid phase, and therefore, a complete understanding of the rheological behavior of slag should allow for the case of "partly crystallized slag," which contains some solid particles. Kondratiev and Jak [72,73] developed a viscosity model for the cases of completely liquid and heterogeneous and partly crystallized, using a semi-empirical model originally introduced by Urbain *et al.* [86] for Al_2O_3-CaO-FeO- SiO_2 systems in equilibrium with metallic iron. Here, the viscosity of the liquid slag was described by the Weymann-Frenkel equation:

$$\eta_L = AT \exp\left(\frac{10^3 B}{T}\right) \tag{3.25}$$

where T is the temperature in degrees Kelvin. A and B are model parameters, depending on the liquid composition, related to each other by:

$$-\ln A = mB + n \tag{3.26}$$

where m and n are model parameters. They represent B as a polynomial function depending on the slag composition, composed of the three groups: G-glass formation (SiO_2) Amphamphoteric oxides (Al_2O_3), and Mod-modifier oxides (CaO-FeO, MgO), such that:

$$B = B_0 + B_1 X_G + B_2 X_G^2 + B_3 X_G^3 \tag{3.27}$$

where:

$$B_i = b_i^0 + b_i^1 \alpha + b_i^2 \alpha^2$$
$$i = 0, 1, 2, 3 \quad \text{and} \quad \alpha = \frac{X_{Mod}}{X_{Mod} + X_{Amph}} \tag{3.28}$$

where X_G, X_{Mod}, and X_{Amph} are the mole fractions of glass formers, modifiers, and amphoteric oxides, respectively. Kondratiev and Jak [72,73] also tested a number of viscosity correlations for the heterogeneous liquids and found that the Roscoe equation [87] is suitable for the cases studied. This equation is appropriate for a colloidal fluid with suspension of rigid spheres of diverse sizes:

$$\eta_S = \eta_L \left(1 - V_S\right)^{-2.5} \tag{3.29}$$

where η_S is the viscosity of slurry and V_S is the volume fraction of solid particles. In this equation, the effects of particle size or shapes are ignored, and it is assumed that the slurry behaves as a Newtonian fluid whose viscosity is given by this equation. According to the experimental results of Wright *et al.* [88], Roscoe's equation can be used for partly crystallized slags. Mudersbach *et al.* [89] also generalized the Urbain model by adjusting the coefficients of Weymann's temperature relation to depend on the CaO/SiO_2 basicity of the slag, namely:

$$\eta = AT \exp\left(\frac{10^3 B}{T}\right) \tag{3.30}$$

where:

$$A = f(C/S - \text{basicity});$$
$$B = f(X_{oxides}) \tag{3.31}$$

Thus, in this model, referred to as the FEhS model, m and n are adjusted to include the effects of the CaO/SiO$_2$ basicity.

Browning *et al.* [15] provide a brief review of the various slag viscosity models, and they observed that the Kamanovitch-Urbain method is the most accurate for SiO$_2$-Al$_2$O$_3$-CaO-MgO slags. They also suggested an empirical method to obtain the viscosity of the slag that depends on finding the temperature shift, among other parameters. For the standard viscosity curve they suggested the following expression:

$$\log\left(\frac{\eta}{T-T_s}\right) = \frac{14788}{T-T_s} - 10.931 \tag{3.32}$$

Thus, if the temperature shift for a given slag composition is known, the above equation can be used to find the viscosity above the T$_{cv}$. They also observed that the temperature shift depends on a weighted molar ratio A, given by the following expression:

$$T_s = 306.63 \ln A - 574.31 \tag{3.33}$$

where A was given by a polynomial expression in which the coefficients or the quantities associated with each component are in terms of the mole fraction. The idea of the temperature shift is based on the observation made by Nicholls and Reid [90] who stated that, at a given viscosity, the gradient of the viscosity-temperature curve is the same as if the coal ash slag is in the Newtonian range.

Inaba and Kimura [91] measured the viscosity of carbon-bearing iron oxide pellets with the acid component of slag by using the oscillating-plate viscometer developed by Iida *et al.* [82]. Specifically, they used the following equation:

$$\rho\mu = K\left(\frac{E_a}{E} - 1\right)^2 \tag{3.34}$$

where:

$$K = \frac{R_M^2}{\pi f_a A^2} \tag{3.35}$$

where ρ is the density (kg/m3), μ is the viscosity (Pa·s), E$_a$ is the amplitude of vibration in the air (m), E is amplitude of vibration in the liquid, R$_M$ the impedance of the viscometer (kg·m/s), f$_a$ is the sympathetic frequency in the air (Hz), and A is the surface area of both sides of the oscillating plate (m2). The exponent 2 was found not to change with different experiments. Nakamoto *et al.* [92] attempted to develop a viscosity model that is non-linear in the concentration of slags. Specifically, they used the concept of "cutting-off" points, which are adjacent to non-bridging oxygen and the free oxygen ions, creating a non-linear network structure. They suggested that the viscosity of the molten slag depends on the frequency of the occurrence of "cutting-off" points and suggested the following Arrhenius-type equation:

$$\eta = A \exp\left(\frac{E_v}{RT}\right) \tag{3.36}$$

where A is a constant and E_V is the activation energy for viscosity, which was assumed to be inversely proportional to the distance S, in which the "cutting-off" point moves when a stress is applied. Thus:

$$E_V = \frac{E'}{S} \tag{3.37}$$

They suggested that for multi-component systems, the activation energy E_V is given by:

$$E_V = \frac{E}{1 + (\alpha_m)^{1/2}} \tag{3.38}$$

where α_m is given by a complicated equation as a function of the number of oxides, the fractions of the non-bridging oxygen, and the free oxygen ions. Buhre *et al.* [93] discuss the method of thermomechanical analysis (TMA) to determine the slag viscosity. In this method, measurements can be made up to 2,400 °C. They showed that:

$$\mu = \frac{mg}{4\pi u(L_0 + d)}\left[\frac{\ln(1/\kappa)(1 + \kappa^2) - (1 - \kappa^2)}{\kappa^2}\right] \tag{3.39}$$

where κ is the ratio of the radius of the ram to the internal radius of the crucible, R is the internal radius of the crucible (in meters), u is the velocity of the ram (m/s), L_0 is the initial length of the annular region, d is the displacement of the ram, m is the mass applied to the rim (kg), and g is the gravity (kg/m^3). The above relationship is the balance between the pressure applied to the ram and the flow rate. Buhre *et al.* [93] emphasize that their results are not valid for the cases in which the molten ash contains solids and, thus, behave as a non-Newtonian fluid. As Seok *et al.* [94] observed, the highly basic BOF slags exhibit much higher viscosities than those measured for normal slags. They suggested using the Einstein-Roscoe equation for the liquid melt containing solid particles:

$$\eta = \eta_0(1 - af)^{-n} \tag{3.40}$$

where η, η_0, and f are the viscosity of the liquid melt with solid particles, without solid particles, and the volume fraction of the particles, respectively. The parameter 'a' is related to the inverse maximum faction of the particles, and the constant n is related to the geometrical shape of the particles and is assumed to be 2.5 for spherical particles. Kalicka *et al.* [95] extended Iida's model for the case of CaF_2 and observed that the presence of this component decreased the slag viscosity strongly.

The conventional ash flow temperature (AFT) analysis only takes into account the bulk chemical composition of the mineral phase; that is, the compositions in the slag-liquid phase are not distinguished from those in the crystallized phase. The AFT is the main parameter that suggests the suitability of a coal type for combustion or gasification and was originally developed to study the clinker forming characteristics of ash in stoker-fired furnaces [96,97]. Van Dyk *et al.* [97] identified two important temperature ranges: (a) between 900 °C and 1000 °C, the slag begins to form; and (b) between 1,000 °C and 1,250 °C, there is a mixture of slag-liquid and crystallized material. They used the modified "Urbain Model" to calculate the viscosities of various slags:

$$\ln\eta = \ln A + \ln T + \frac{1000\,B}{T} \tag{3.41}$$

where:

$$\ln A = -(.2812\ B + 11.8279) \tag{3.42}$$

$$B = B_0 + B_1 SiO_2 + B_2 (SiO_2)^2 + B_3 (SiO_2)^3 \tag{3.43}$$

where the Bs are given polynomial functions of α where:

$$\alpha = \frac{M}{M + Al_2O_3} \quad \text{mole fraction}$$
$$M = CaO + MgO + Na_2O + K_2O + FeO + 2TiO_2 \quad \text{mole fractions} \tag{3.44}$$

It was observed that the viscosity decreases as the CaO content increases [96].

Another area of similar behavior or response between molten steel and slag is the viscoelastic response of such materials, where, at high temperatures, the time dependent constitutive relations are needed not only for the stress-stress relationship, but also for the heat flux vector. In an important paper Kozlowski *et al.* [38] suggested four types of elastic-viscoplastic constitutive relations of the type:

$$\dot{\varepsilon}_p = \dot{\varepsilon}_p(\sigma, \theta)$$
$$\dot{\varepsilon}_p = \dot{\varepsilon}_p(\sigma, \theta, t)$$
$$\dot{\varepsilon}_p = \dot{\varepsilon}_p(\sigma, \theta, \varepsilon_p) \tag{3.45}$$
$$\dot{\varepsilon}_p = \dot{\varepsilon}_p(\sigma, \theta, \varepsilon_p, t)$$

where they suggested using the standard Hooke's law for the stress-strain relationship, *i.e.*:

$$\dot{\sigma} = E\dot{\varepsilon}_e \tag{3.46}$$

where:

$$\dot{\varepsilon} = \dot{\varepsilon}_e + \dot{\varepsilon}_p + \dot{\varepsilon}_\theta \tag{3.47}$$

where $\dot{\sigma}$ is the stress rate, $\dot{\varepsilon}$ is the total strain rate, $\dot{\varepsilon}_e$ is the elastic strain rate, $\dot{\varepsilon}_p$ is the inelastic (plastic) strain rate, $\dot{\varepsilon}_\theta$ is the thermal strain rate, and θ is the temperature in Kelvin. A significant contribution of this work was the recognition of the difficulty of measuring and the importance that the Young's modulus E plays in this kind of problem. They used the experimental results of Mizukami *et al.* [98], where:

$$E[GPa] = 968 - 2.33(\theta - 273) + 1.90 \times 10^{-3}(\theta - 273)^2 - 5.18 \times 10^{-7}(\theta - 273)^3 \tag{3.48}$$

This equation is valid for the range of 900 °C and the liquidus. For the four mentioned models, Kozlowski *et al.* [38] suggested various constitutive relations for $\dot{\varepsilon}_p$ as functions of stress, temperature, carbon content, activation energy, and various adjustable parameters such as temperature dependent stress exponent, *etc.* (see also Thomas [99,100] for a review of this subject). In the continuous casting of steel, when mold powder is added to the free surface of the liquid steel, it begins to melt and flow. The re-solidified mold powder, also called slag forms a layer adjacent to the walls; there is an increase in its viscosity and it begins to act as a solid-like material [101,102]. Once the slag cools, it creates a glassy layer. Heat conduction across the slag layer plays a major role in the operation; it is a function of the thickness of the slag and depends on the conductivity of the various layers and particles embedded in

the slag. In the model that they developed, Meng and Thomas [101] suggested that the viscosity of molten slag depends on the temperature in the following way:

$$\mu(\theta) = \mu_0 \left(\frac{\theta_0 - \theta_{fsol}}{\theta - \theta_{fsol}} \right)^n \tag{3.49}$$

where θ_{fsol} and n are empirical constants chosen to fit the measured data, μ_0 is a reference viscosity measured at the reference temperature, and θ_0 is usually chosen to be 1,300 °C [19]. Meng and Thomas [102] suggested that shear stress in the liquid slag can be represented by:

$$\tau_{xz} = \mu \frac{\partial v_z}{\partial x} \tag{3.50}$$

where μ is given by the above equation, while recognizing that in the slag layer the viscosity can be represented by a position-dependent function such that:

$$\tau_{xz} = \mu_0 \frac{d_l^n}{x^n} \frac{\partial v_z}{\partial x} \tag{3.51}$$

where d_l is the liquid film thickness. In the continuous casting of steel, it has been observed that the viscosity of the molten slag or flux varies with the composition of the various elements present and the temperature. For example, most commercial fluxes contain (0–13%) Al_2O_3, (22%–45%) CaO , and (17%–56%) SiO_2, with small amounts of fluorides (NaF, CaF_2), alkalis (Na_2O, K_2O) and other basic oxides (MgO, BaO) , [19]. It is well known that the viscosity of liquid flux can be represented by an Arrhenius equation of the following type:

$$\mu = A \exp\left(\frac{E}{R\theta} \right) \tag{3.53}$$

As the powder sinters, its viscosity is increased greatly. Riboud and Larrecq [71] suggest an alternative equation:

$$\mu = A\theta e^{B/\theta} \tag{3.54}$$

where:

$$\ln A = -20.81 - 35.75 x_{Al_2O_3} + 1.73 x_{CaO} + 5.82 x_{CaF_2} + 7.02 x_{Na_2O}$$
$$B = 31140 + 68833 x_{Al_2O_3} - 23896 x_{CaO} - 46351 x_{CaF_2} - 39519 x_{Na_2O} \tag{3.55}$$

where μ is the viscosity measured in Pa·s, θ is the temperature in degree Kelvin, and x is the mole fraction of the constituent. For a typical flux [19], B is ~24,000. To study for a range of fluxes, Zhao *et al.* [19] suggested an equation of the type:

$$\mu = \mu_0 \frac{\theta}{\theta_0} e^{B\left(\frac{1}{\theta} - \frac{1}{\theta_0}\right)} \tag{3.56}$$

where θ_0 is a reference temperature (1,773 K), μ_0 is a reference viscosity (0.05 Pa·s) and B is a parameter representing the temperature dependency of the flux viscosity.

Table 1. Examples of viscosity of the slag as a function of temperature, time, chemical composition, concentration, and shear rate.

Viscosity as a function of temperature	See for example Equations (3.1), or (3.2), and others. Generally expressed as an exponential function or some type of power-law [see Equation (3.49)]
Viscosity as a function of time	See Equation (3.5)
Viscosity as a function of chemical composition	See Equations (3.9)–(3.12) and others. Generally expressed as a polynomial equation
Viscosity as a function of concentration	See Equation (3.13), generally expressed as a polynomial [see also Table 2 in Section 4]
Viscosity as a function of the shear rate	See Equation (3.50), generally expressed as the power-law type non-Newtonian fluid model

From this brief review in this section, it can be seen that the majority of applications have been concerned with the dependency of slag on temperature, time, chemical composition, concentration and shear rate [see Table 1]. In the next section of this paper, we discuss various existing constitutive models for non-linear viscoelastic materials that can be used to model the rheological characteristics of slag.

4. Constitutive Modeling of Slag

As evidenced in Section 3 of this paper, the viscosity of slag is the most important parameter in determining the proper operating conditions for a gasifier. However, viscosity is only one of the important rheological parameters and since slag, in general, behaves as a non-linear fluid, we must study the constitutive modeling of slag. That is, if we know how the slag viscosity changes as a function of temperature, concentration, shear rate, *etc.*, we still do not know much about the complete rheological characteristics or behavior of the slag, but only its shear viscosity or response. Whether the slag has a yield stress, or exhibits normal stress effects, or is able to demonstrate stress relaxation or creep, are questions that can only be answered if one provides constitutive models for the complete behavior of slag, and not just its response in shear.

4.1. Background

The stress tensor and the heat flux vector are two important constitutive relations needed to study flow and heat transfer in complex fluid-like materials (ignoring the effects of radiation). From an engineering perspective, this oftentimes translates into measuring viscosity and thermal conductivity. As a result, most researchers have attempted to generalize Newton's law of viscosity and Fourier's law of heat conduction to various and more complicated cases by assuming that the shear viscosity and/or thermal conductivity could depend on a host of parameters, such as shear rate, temperature, porosity, *etc.* A more rigorous approach is to model the stress tensor and the heat flux vector.

While a constitutive equation is a postulate or a definition from the mathematical standpoint, physical experience remains the first guide, perhaps reinforced by experimental data. Constitutive relations are also required to satisfy some general principles. Wang and Truesdell ([103], p. 135) list six general principles: (1) Determinism, (2) Local action, (3) Equipresence, (4) Universal dissipation,

(5) Material frame-indifference, and (6) Material symmetry. The principle of material frame-indifference (sometimes referred to as Objectivity), which requires that the constitutive equations be invariant under changes of frame, is perhaps the most important of all. This principle is a consequence of the classical physics principle that states material properties are independent of the observer's frame of reference. It requires that constitutive relations depend only on frame-indifferent forms (or combinations thereof) of the variables pertaining to the given problem. In general, based on available experimental observations, many slags exhibit characteristics similar to those of non-linear materials. The main points of departure from linear behavior are:

1. The ability to shear-thin or shear-thicken
2. The ability to creep
3. The ability to relax stresses
4. The presence of normal stress differences in simple shear flows
5. The presence of yield stress

The non-linear time-dependent response of complex fluids constitutes an important area of mathematical modeling of non-Newtonian fluids. For many practical engineering cases, where complex fluids such as paint and slurries are used, shear viscosity can be a function of one or all of the following: time, shear rate, concentration, temperature, pressure, electric field, magnetic field, *etc.* Thus, in general:

$$\mu = \mu(t, \pi, \theta, \phi, p, \mathbf{E}, \mathbf{B}, ...) \tag{*}$$

where t is the time, π is some measure of the shear rate, θ is temperature, ϕ is concentration, p is pressure, $\mathbf{E}$ is electric field, and $\mathbf{B}$ is the magnetic field. Of course, in certain materials or under certain conditions, the dependence of one or more of these can be dropped. It is not clear whether a slag layer would exhibit all of the possible five non-linear responses listed above. However, based on the results available, it is clear that a few of these non-linear effects have been observed for slags.

This section of the paper is not intended to be comprehensive of all existing models, but rather the aim is to be representative and discuss a few sample cases.

4.2. Yield Stress

Although it has been recognized that the slag behaves as a yield stress type fluid, in most papers that were mentioned in Section 3 of this paper, it was taken for granted that the slag behaves as a Bingham-type fluid. In this sub-section we briefly discuss this model and point out that for a slag layer, another important parameter should be incorporated. This parameter is the temperature of the critical viscosity, T_{cv} defined as the temperature where the behavior of the molten ash changes from a Newtonian fluid to that of a non-Newtonian fluid, specifically a Bingham fluid [74,75].

Bingham ([104], p. 215) proposed a constitutive relation for a visco-plastic material in a simple shear flow where the relationship between the shear stress (or stress **T** in general), and the rate of shear (or the symmetric part of the velocity gradient **D**) is given by the following (see Prager [105], p. 137):

$$2\mu D_{ij} = \begin{cases} 0 & \text{for} \quad F < 0 \\ FT'_{ij} & \text{for } F \geq 0 \end{cases} \tag{4.1}$$

where T_{ij}' denotes the stress deviator and F, called the yield function, is given by:

$$F = 1 - \frac{K}{II_2'^{1/2}}$$

(4.2)

where II_2' is the second invariant of the stress deviator, and in simple shear flows it is equal to the square of the shearing stress and K is called yield stress (a constant). For one-dimensional flow, these relationships reduce to the ones proposed by Bingham [104]:

$$F = 1 - \frac{K}{|T_{12}|}$$

(4.3)

and:

$$2\mu D_{12} = \begin{cases} 0 & \text{for} F < 0 \\ FT_{12} & \text{for} F \geq 0 \end{cases}$$

(4.4)

The constitutive relation (2a.1) is known as the Bingham model (see also Ziegler [44], p. 170). Casson [106] considered that the suspended particles flocculate into rod-like structures, which are broken into primary particles as the shear rate increases. He then developed the following widely used empirical model for the tension in rods under flow:

$$\tau^{1/2} = \tau_O^{1/2} + \mu_\infty^{1/2} \gamma^{1/2}$$

(4.5)

In this equation τ_o is the yield stress, μ_∞ is the suspension viscosity at infinite shear rate and γ is the shear rate. One of the inherent limitations of such empirical models is that they are, in general, one-dimensional, and it is not that easy or straightforward to generalize and obtain the appropriate three-dimensional forms, which are often necessary to solve general three-dimensional problems. Nevertheless, this equation has been successful for a range of parameters and a class of fluids. Oldroyd [107] proposed the following generalization of the Bingham solid [108]:

$$T_{ij} = p\delta_{ij} + (\mu + \frac{\tau_0}{|D_{ij}|})D_{ij}$$

(4.7)

In a coal-water paste (CWP) atomization system with a high concentration of coal and wide particle size distribution, such as those used in pressurized fluidized-bed combustion (PFBC) facilities, the CWP is often modeled as a Herschel-Bulkely model (see Tanner [109], p. 146) where the effect of yield (using Bingham plastic type model) and shear-rate dependence (using the Power-law model) are combined:

$$T_{ij} = 2\mu_0 D_{ij} \text{when} \dot{\gamma} \leq \dot{\gamma}_c$$

(4.8)

$$T_{ij} = 2\left\{ \frac{\tau_\gamma}{\dot{\gamma}} + k|\dot{\gamma}|^{n-1} \right\} D_{ij} \text{when} \dot{\gamma} > \dot{\gamma}_c$$

(4.9)

where $\dot{\gamma}_c$ is a critical shear rate. There are obviously other yield criteria which can be used. For example, by including the gradient of the volume fraction as one of the important parameters in proposing a constitutive equation for the stress tensor, a theory could be devised for the flow of

granular materials (see Massoudi and Mehrabadi [110]). In this theory a critical yield condition called the Mohr-Coulomb emerges naturally, as does the transition between the frictional flow regimes, characterized by the absence of deformation and the viscous flow regime, characterized by deformation. More work is needed in this area before an appropriate yield-stress can be formulated for slags.

4.3. Effects of Concentration, Shear Rate, and Pressure

We will not discuss the effects of temperature on the viscosity as this was the main emphasis in Section 3 of this paper.

4.3.1. Concentration Effect

As we saw in Section 3, there were a few examples where the viscosity was assumed to depend on the concentration, for example, Equations (3.13), (3.29), and (3.40), all of which were polynomial functions of some type. However, as we discuss in this sub-section it is possible to have other types of dependency.

The problem of theoretical determination of the viscosity of a dilute suspension consisting of an incompressible Newtonian fluid and rigid sphere particles was studied by Einstein [57] who derived the classical formula for the effective viscosity of the suspension:

$$\mu = \mu_f \left(1 + 2.5\phi\right) \qquad (4.10)$$

where μ_f is the viscosity of the fluid base and ϕ is the particle volume fraction, which was assumed to be very small compared with unity. Later, Taylor [58] showed that if the spheres are small drops of another fluid, then the viscosity of the suspension is given by:

$$\mu = \mu_f \left[1 + 2.5\phi \left(\frac{\mu_d + \dfrac{2\mu_f}{5}}{\mu_d + \mu_f} \right) \right] \qquad (4.11)$$

where μ_d is the viscosity of the liquid drops and μ_f is the viscosity of the base fluid. Batchelor and Green [111] considered the effect due to the Brownian motion of particles for an isotropic suspension of rigid sphere and spherical particles. They derived a formula for the effective viscosity including the terms of order ϕ^2 and showed that:

$$\mu = \mu_f \left(1 + 2.5\phi + 7.6\phi^2\right) \qquad (4.12)$$

where $\phi < 1$. The non-linear dependence of the viscosity on the particle volume fraction observed here indicates significant interparticle interaction. To account for such interactions, Brinkman [112], Roscoe [87], Krieger and Dougherty [113], Nielsen [114], and Mooney [115] used the differential effective medium approach for hard sphere suspension to extend Einstein's formula to a moderate particle volume fraction of about 0.04. Some of these models are:

Table 2. Additional correlations for the viscosity as a function of concentration.

Mooney (1951) [115]	$\mu = \mu_f \exp\left[\dfrac{2.5\phi}{1 - K\phi}\right]$ [Equation (4.13)] where K is the crowding factor	
Roscoe (1952) [87]	$\mu = \mu_f (1 - \phi)^{-2.5}$ [Equation (4.14)]	
Brinkman (1952) [112]	$\mu = \dfrac{\mu_f}{(1 - \phi)^{2.5}}$ [Equation (4.15)]	
Krieger and Dougherty (1959) [113]	$\mu = \mu_f \left(1 - \dfrac{\phi}{\phi_m}\right)^{-2.5\phi_m}$ [Equation (4.16)]	
Nielsen (1970)[114]	$\mu = \mu_f (1 + 1.5\phi) e^{\phi/(1-\phi_m)}$ [Equation (4.17)]	
Choi *et al.* (2000) [116], Kwon *et al.* (1998) [117]	$\ln\left(\dfrac{\mu}{\mu_f}\right) = \dfrac{\mu_\infty \phi}{1 - \phi/\phi_m}$; non-spherical particles where ϕ_m is the maximum packing volume fraction. [Equation (4.18)]	

4.3.2. Normal Stress Effects and Shear-Rate Dependent Viscosity

Surprisingly, in all the papers studied in Section 3, there was no discussion on the possibility that the slag can exhibit normal stress effects. Perhaps the simplest constitutive model which can capture the normal stress effects (which could lead to phenomena such as "die-swell" and "rod-climbing"—manifestations of the stresses that develop orthogonal to planes of shear) is the second grade fluid, or the Rivlin-Ericksen fluid of grade two [45,118]. This model has been used and studied extensively [119] and is a special case of differential-type fluids. For a second grade fluid, the Cauchy stress tensor is given by:

$$\mathbf{T} = -p\mathbf{1} + \mu\mathbf{A_1} + \alpha_1\mathbf{A_2} + \alpha_2\mathbf{A_1}^2 \tag{4.19}$$

where p is the indeterminate part of the stress due to the constraint of incompressibility, μ is the coefficient of viscosity, α_1 and α_2 are material moduli, which are commonly referred to as the normal stress coefficients. The kinematical tensors $\mathbf{A_1}$ and $\mathbf{A_2}$ are defined through:

$$\mathbf{A_1} = \mathbf{L} + \mathbf{L^T}$$

$$\mathbf{A_2} = \frac{d\mathbf{A_1}}{dt} + \mathbf{A_1}\mathbf{L} + (\mathbf{L})^\mathbf{T}\mathbf{A_1} \tag{4.20 a,b,c}$$

$$\mathbf{L} = \text{grad}\,\mathbf{u}$$

The thermodynamics and stability of second grade fluids have been studied in detail by Dunn and Fosdick [119]. They show that if the fluid is to be thermodynamically consistent in the sense that all motions of the fluid meet the Clausius-Duhem inequality and that the specific Helmholtz free energy of the fluid is a minimum in equilibrium, then:

$$\begin{aligned} \mu &\geq 0, \\ \alpha_1 &\geq 0, \\ \alpha_1 + \alpha_2 &= 0 \end{aligned} \tag{4.21 a,b,c}$$

For such fluids, orthogonal rheometers are needed to measure the normal stress coefficients and these tests/experiments are in addition to the traditional shear viscometers which can only provide information about the shear viscosity. In an effort to obtain a model that does exhibit both normal stress effects and shear-thinning/thickening, Man [120] modified the constitutive equation for a second grade fluid by allowing the viscosity coefficient to depend upon the rate of deformation. The two proposed models are [121]:

$$\mathbf{T} = -p\mathbf{1} + \mu \Pi^{m/2} \mathbf{A_1} + \alpha_1 \mathbf{A_2} + \alpha_2 \mathbf{A_1^2} \tag{4.22a}$$

$$\mathbf{T} = -p\mathbf{1} + \Pi^{m/2}\left(\mu \mathbf{A_1} + \alpha_1 \mathbf{A_2} + \alpha_2 \mathbf{A_1^2}\right) \tag{4.22b}$$

where:

$$\Pi = \frac{1}{2} \mathrm{tr}\mathbf{A_1^2} \tag{4.23}$$

is the second invariant of the symmetric part of the velocity gradient, and m is a material parameter. When m < 0, the fluid is shear-thinning, and if m > 0, the fluid is shear-thickening; in Equation (4.22a) only the shear viscosity depends on the shear rate, whereas in Equation (4.22b) the viscosity and the normal stress coefficients are dependent upon shear rate. A subclass of models given by Equation (4.22) is the generalized power-law model, which can be obtained by setting $\alpha_1 = \alpha_2 = 0$:

$$\mathbf{T} = -p\mathbf{1} + \mu_0 \left(\mathrm{tr}\mathbf{A_1^2}\right)^m \mathbf{A_1} \tag{4.24}$$

The power-law models are deficient in many ways: they cannot predict the normal stress differences or yield stresses; they cannot capture the memory or history effects. At the same time, the power-law models have been used for a variety of applications where the shear viscosity is not constant [41,122,123]. Gupta and Massoudi [124] generalized the model given by Equation (4.22 a), by allowing the shear viscosity to be a function of temperature:

$$\mathbf{T} = -p\mathbf{1} + \mu(\theta)\prod^{m/2} \mathbf{A_2} + \alpha_1 \mathbf{A_2} + \alpha_2 \mathbf{A_1^2} \tag{4.25}$$

where $\mu(\theta)$ was assumed to obey the Reynolds viscosity model [125]:

$$\mu(\theta) = \mu_0 e^{-M\theta} \tag{4.26}$$

where $M = n(\theta_2 - \theta_1)$. This is a general model applicable to many chemical processes.

4.3.3. Pressure Effects

For many fluids (known as the rate-dependent models, such as Maxwell or Oldroyd models) the rate of the stress tensor **T** is described implicitly as a function of **T** and **D**. Another class of implicit constitutive theories have been proposed by Rajagopal and co-workers, where:

$$\mathbf{T} = -p\mathbf{1} + \rho v\mathbf{D} \tag{4.27}$$

where $v = v(p, |\mathbf{D}|^2)$. Franta *et al.* [126] considered a class of incompressible fluids where viscosity depends not only on pressure but also on shear rate. They considered the following forms for the kinematic viscosity:

$$\nu_i(p, |\mathbf{D}|^2) = \left[A + \gamma_i(p) + |\mathbf{D}|^2\right]^{\frac{(r-2)}{2}}; \qquad i = 1,2,3 \qquad (4.28)$$

where $A \in (0,1]$ and $r \in (1,2)$ are constants and γ_i is given by any of the relationships:

$$\gamma_1(p) = (1 + \alpha^2 p^2)^{-q/2}$$

$$\gamma_2(p) = \left[1 + \exp(\alpha p)\right]^{-q} \qquad (4.29 \text{ a,b,c})$$

$$\gamma_3(p) = \begin{cases} \exp(-\alpha q p) & \text{if } p > 0 \\ 1 \end{cases}$$

where α and q are constants. They also noted that when r = 2, all the possible correlations for viscosity given by Equation (4.28) reduce to the classical Navier-Stokes viscosity, and when $r \neq 2$, q = 0, or $\alpha = 0$, the viscosity depends on the second invariants of **D,** and the model becomes a special case of the general Stokesian fluid. Hron *et al.* [127] suggested the following:

$$\mathbf{T} = -p\mathbf{1} + 2\mu(p)|\mathbf{D}|^{n-2}\mathbf{D} \qquad (4.30)$$

where, when n = 2, this model reduces to $\mathbf{T} = -p\mathbf{1} + 2\mu(p)\mathbf{D}$. When $n \in < -1, 2)$, the fluid is a shear thinning, and when n > 2, a shear-thickening. This equation is perhaps the simplest form of a pressure-dependent viscosity fluid.

In the final section of this paper, we present a few remarks about modeling issues related to slag viscosity. We also propose a simple yet general constitutive relation, which we think would be appropriate for slags.

5. Concluding Remarks

In this paper we have attempted to provide a review of the various possible ways of formulating the viscosity of slag as reported in the literature. In our opinion, a major shortcoming of these studies is that the emphasis has been put on the meaning or the measurement of the shear viscosity. In reality, however, the issue is: What constitutive equation would be a reasonable or a more appropriate representation for the stress tensor for the slag? With this perspective, the emphasis shifts to constitutive modeling of the slag as a whole and not just the measurement of slag viscosity, and as a result, with experiments as the basis of the development, we need to formulate models for slag in specific applications. Interestingly, materials that apparently have nothing in common can be expressed rheologically in a similar manner. For example, many studies indicate that for lava (Griffiths [128]) or coal slurries [129] viscosity is a function of temperature, volume fraction, and size and shape of the particles. In many applications, for example melt fraction [130] and basaltic lavas, the apparent viscosity is assumed to follow the Einstein-Roscoe relation [87,131]:

$$\eta(\theta, \phi) = \eta_0 \left(1 - \frac{\phi}{\phi_{max}}\right)^{-2.5} e^{\gamma(\theta_0 - \theta)} \qquad (5.1)$$

where ϕ_{max} is the maximum crystal fraction in which flow can occur, θ_0 and η_0 are reference values, and γ is a constant.

Based on the experimental evidence and the review presented in this paper, it is clear that a general constitutive relation for the slag should at the very least be able to predict (or include) some type of yield stress and a viscous stress with shear-thinning capabilities, *i.e.*, where the coefficient of viscosity not only depends on the shear rate, but also on concentration, temperature, *etc.* Thus, we propose:

$$\mathbf{T} = \mathbf{T}_y + \mathbf{T}_v \tag{5.2}$$

where in general, the yield stress can be obtained from experiments [see Section 4.2] and for the viscous stresses we suggest a model where the material exhibits normal stress effects and the shear viscosity depends on volume fraction, temperature, chemical composition and shear rate [132] where [see Sections 3, Sections 4.3.1 and 4.3.2]:

$$\mathbf{T}_v = -p\mathbf{1} + \mu(\theta, \varphi, X_\alpha)\Pi^{m/2}\mathbf{A}_1 + \alpha_1\mathbf{A}_2 + \alpha_2\mathbf{A}_1^2 \tag{5.3}$$

where the specific form of the viscosity $\mu(\theta, \varphi, X_\alpha)$ is given by appropriate equation based on the experimental data available and α_1 and α_2 are the material moduli, which are commonly referred to as the normal stress coefficients; Also $\Pi = \dfrac{1}{2}\text{tr}\mathbf{A}_1^2$ is the second invariant of the symmetric part of the velocity gradient, and m is a material parameter. When m < 0, the fluid is shear-thinning, and if m > 0, the fluid is shear-thickening. This model is a general frame invariant model, suitable for flows of non-linear fluids with the viscosity being a function of temperature, concentration, and shear rate, and the material exhibiting both normal stress differences. Obviously the methodology that we have presented here is not very rigorous. Of course, in the studies reviewed here, the concept of normal stress was not discussed, and it is not known whether some or none of the various kinds of slag would exhibit normal stress effects. The measurement of these material parameters presents new opportunities for the slag community.

Finally, among the challenging problems in understanding the flow and behaviour of slag, one can name the particle-slag interaction. Whether a carbon-containing particle of a given size would settle at the boundary on the slag layer or get entrapped inside the slag depends on many factors, such as the angle of contact, slag viscosity, forces acting on the particle, *etc.* [133,134]. Another important parameter in understanding and controlling the slag layer is the surface tension of molten slag, which is especially significant in the refining or continuous-casting process of making steel [135]. The slag layer could potentially cause degradation of the refractory liner. Chemical dissolution, erosion, chemical spalling and structural spalling are among the important parameters affecting the mechanism involved in the slag-refractory in a gasifier [136]. The removal of nonmetallic inclusions using direct absorption methods into the slag layer is an important problem in steelmaking industries. Among the important forces influencing this process are drag, capillary, and fluid added mass. Shannon *et al.* [133,134] suggested using the Brenner drag model, which like many other drag models includes the viscosity of slag. When there is contact between an oxide particle and a molten oxide slag phase, at least two important phenomena occur [137]: (1) how the particle responds and whether it settles into the slag (depending on the interaction forces, especially drag, capillary, added mass, *etc.*) and (2) whether the particle will dissolve into the slag, depending on the slag and oxide properties, particle concentration, *etc.*

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