PREDICTION OF PHASE EQUILIBRIA AND VISCOSITY IN COMPLEX COAL ASH SLAG SYSTEMS

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Abstract

Significant improvements in predictive capabilities in relation to the melting behaviour of the mineral matter in coal have been achieved through the use of i) thermodynamic modelling of phase equilibria, and ii) viscosity modelling studies.

The thermodynamic modelling has been carried out using the computer system FactSage, which is used for the calculation of multi-phase slag / solid / gas / matte / alloy / salt equilibria in multi-component systems of industrial interest. A modified quasi-chemical solution model is used for the liquid slag phase. New model optimisations have been carried out, which have significantly improved the accuracy of the thermodynamic models for coal combustion processes. The database for the Al-Ca-Fe-O-Si system has recently been extended to characterise effects of Mg, K and Na. Viscosity modelling, using a modified Urbain formalism, is carried out in conjunction with FactSage calculations to predict the viscosities of fully liquid as well as heterogeneous, partly crystallised slags.

The solution of a range of problems in coal utilisation technologies, including ash slag flow in slagging gasifiers, deposit formation, slagging, fouling, fusibility tests, fluxing, blending etc related to the melting behaviour of the mineral matter in the coal can be obtained with the assistance of the new models.

Introduction

Many coal companies and electrical power utilities are faced with difficult technical issues associated with the melting and flow behaviour of coal mineral matter. A range of problems in coal utilisation technologies, including ash slag flow in slagging gasifiers, deposit formation, slagging, fouling, fusibility tests, fluxing, blending etc, are related to the melting behaviour of the mineral matter in the coal. The wide ranges of coal mineralogies, ash compositions and process conditions experienced in the various parts of each reactor and in different coal utilisation technologies highlight the need for powerful tools to predict the behaviour of the mineral matter. Fundamental knowledge of the melting and flow behaviour of coal mineral matter/flux mixtures can greatly assist in the design and operation of these power generation technologies.

The prediction of phase equilibria and viscosities of the coal ash following combustion is a longstanding problem for users of various coal-based power generation technologies. The empirical "ash fusion tests", such as the cone deformation tests, thermo-mechanical tests (e.g. TMA) and empirical slagging indices are widely used to estimate and compare the relative behaviours of coal ashes. Recent scientific approaches to the prediction of these properties are, however, starting to produce results that will have a significant impact on the industry. Improvements in chemical thermodynamic and viscosity models of oxide systems, the development of computational methods, computer software and hardware now make it possible to predict the phase equilibrium and flow behaviour in complex multi-component coal ash slag systems. The purpose of this paper is to demonstrate how the latest advances in chemical thermodynamic and viscosity modelling can be used to characterise the melting and flow behaviour of mineral matter present in coal combustion systems.

Development of modelling tools

FactSage Database. One of the predictive tools used successfully in coal ash applications is the computer package FactSage[1]. FactSage is used worldwide in various industries to predict chemical equilibria, the proportions of liquid and solid phases as a function of temperature, composition and atmospheric conditions. One of the strengths of FactSage is its ability to describe the melting behaviour of the oxide systems, commonly referred to as slags. Accurate and reliable prediction, however, requires the development of a thermodynamic database with model parameters for all possible liquid and solid phases.

A new thermodynamic database of the system Al-Ca-Fe-O-Si has been completed by researchers at the Pyrometallurgy Research Centre (PYROSEARCH), The University of Queensland, in collaboration with the Centre for Research in Computational Thermochemistry, Polytechnique de Montreal, Canada[2]. This database has recently been extended to characterise effects of Mg, K and Na on liquidus temperatures[3-4]. The new thermodynamic database incorporates the latest experimental data and more advanced thermodynamic models of the oxide phases. The new database is the result of the systematic thermodynamic optimisation of the multi-component systems, and it provides improved accuracy and reliability in the description of phase equilibria in the coal ash system.

Viscosity Model. A new slag viscosity model for the system Al_2O_3-CaO-'FeO'-SiO_2 used in conjunction with FactSage has recently been completed by the present authors[5-7]. The model enables the viscosities of homogeneous (completely molten) liquid slag systems as well as heterogeneous (partially crystallised) slag systems, to be predicted as a function of the bulk slag composition and operating temperature over the complete range of conditions at metallic iron saturation. FactSage is used to calculate the proportions of solids and the composition of the remaining liquid in the partly crystallised slag systems. The original Urbain formalism[8-11] has been modified to make viscosity predictions possible over the whole composition and temperature ranges. This was achieved by taking into account the different contributions of various oxides (in this particular case, CaO and FeO) on the viscosity of the slag[6]. The model parameters for the individual oxides have been derived from critically reviewed experimental data. The Roscoe equation[12], with parameters obtained by fitting model predictions into experimental points by Hurst[13-15], is used to characterise the "slurry" effect in partly crystallised slag. Examples of the application of the new viscosity model have been reported in the literature[5-7].

Table 1. Comparison of Different Viscosity Models Using the Mills' Parameter

System	Modified Urbain model[5-7]	Watt-Fereday model[17]	T-shift model[18]	Kalmanovich-Frank model[19]
SiO_2	19.1	99.9	N/A	99.9
Al_2O_3-SiO_2	30.1	66.9	N/A	41.5
CaO-SiO_2	10.9	84.3	40.3	24.3
'FeO'-SiO_2	8.1	213.8	378.1	717.6
Al_2O_3-CaO-SiO_2	31.2	49.5	49.2	24.6
CaO-'FeO'-SiO_2	9.9	115.4	339.8	594.4
Al_2O_3-CaO-'FeO'-SiO_2	29.2	96.0	94.0	169.6

The agreement between experimental data and model predictions was evaluated using the parameter proposed by Mills et al.[16]: $\Delta = \frac{1}{N}\sum^{N}\left|\frac{(\eta_n)_{calc} - (\eta_n)_{ex}}{(\eta_n)_{ex}}\right|$, where N is a number of points and n is a particular slag system, the subscripts *calc* and *ex* refer to the calculated and experimental viscosities at a given composition and process condition. Table 1 shows the comparison of the viscosity models[5-7,17-19] for a number of chemical systems.

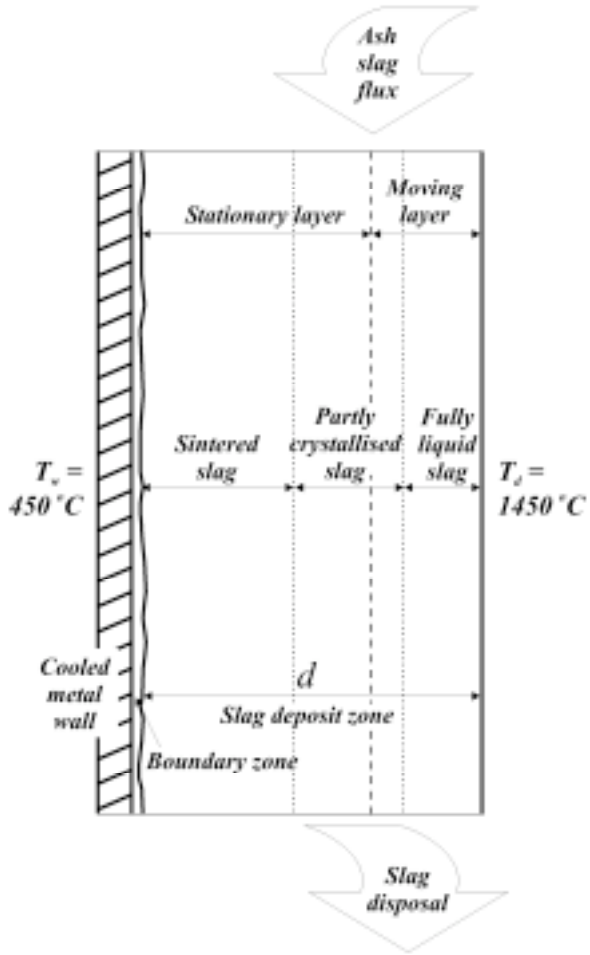

Figure 1. Schematic of the flowing slag deposit.

Applications of the models to entrained flow coal gasification systems

A number of examples of the application of the FactSage computer package and viscosity models to coal ash related problems by the authors can be found in recent scientific literature[2,3,5,20-25]. Increasing attention is being given to the development of entrained flow coal (slagging) gasifiers since they offer potential advantages in terms of improved energy efficiencies and environmental outcomes. A key factor in the operation of these technologies is the flow properties of the slags; these properties are principally dependent on

- liquid composition,
- proportion of liquid,
- proportion of solids,
- oxygen partial pressure, and
- temperature.

These in turn can be controlled or varied in the process by adjustments to

- coal blending,
- flux addition and
- gasifier temperature and operating oxygen partial pressure.

Depending on the gasifier type, the limiting requirements for slag viscosity and temperature can vary from 5 to 25 Pa.s and from 1100°C to 1500°C, respectively[26-28]. These requirements are usually determined empirically by the tappability of the slag in a gasifier. Exact specifications should be identified by individual power generation utilities. Provided the slag can flow from the reactor, and can also fulfil any requirements, such as the incorporation of other minor elements, then it is possible to operate at sub-liquidus conditions.

Using the new thermodynamic and viscosity models described above it is now possible to predict the stability of the liquid slag and solid crystalline phases as well as the viscosity of the liquid slag for the complex coal ash slag systems. This is illustrated in the present paper with analysis of the use of two coals A and B (see Table 2) in a slagging gasifier.

Table 2. Compositions of the Coal Ash Slags (wt pct)

#	Al_2O_3	CaO	'FeO'	SiO_2
Ash A	25.44	27.53	12.50	34.53
Ash B	30.51	25.87	6.26	37.36

One of the common problems in coal gasification is the formation of slag deposit on the walls of a slagging gasifier; these deposits affect the overall heat balance, temperature of the out-gases and tappability of slag (i.e. ability of slag to flow freely from a gasifier)[26,29-30]. The following example shows the application of the thermodynamic and viscosity models developed in the Pyrosearch Centre to the problem of deposit formation in the slagging zone of a gasifier.

A typical section of flowing slag deposit on a reactor wall in the slagging zone[29] is shown in Figure 1. The temperature of the slag at the water-cooled wall of a gasifier T_w is taken ~450°C, while temperature of the slag surface T_d is ~1450°C. The temperature gradient across the slag deposit leads to the formation of different sub-layers across the deposit: 1) a stationary layer of sintered slag (glass and crystalline phases) and partly crystallised slag with high proportion of solids, and 2) a moving layer, which also contains partly liquid slag but with lower percentage of solids, and fully liquid slag. Assuming the linear temperature profile across the slag layer, the proportion of solids across the layer was calculated by FactSage[1] with the new thermodynamic database[4]. The slurry viscosity was predicted by the model developed in PyroSearch Centre[5-7]. Using the Navier-Stokes equation for steady-state, laminar flow of a slag layer of constant thickness under gravity force the slag velocity across the layer was predicted. Thickness of the deposit layer was then calculated from mass balance and geometry of a gasifier. The examples of these calculations for two different coal ash slags (marked Ash A and Ash B) are shown in Figure 2.

Figure 3 shows the thickness of the deposit layer for coal ash slags A and B as a function of the temperature of slag surface determined by the temperature of the reaction zone. It can be seen that ash A has wider operational range of temperatures than ash B.

The conditions of the operations always fluctuate. The analysis of the effects of different factors on crystallisation and viscous flow behaviour therefore is important. Figures 4 through 6 give detailed analysis of the effects of temperature, atmospheric conditions(reducing / oxidising) and composition changes on proportions of liquid and solid phases and on viscosities of the slags corresponding to coals A and B.

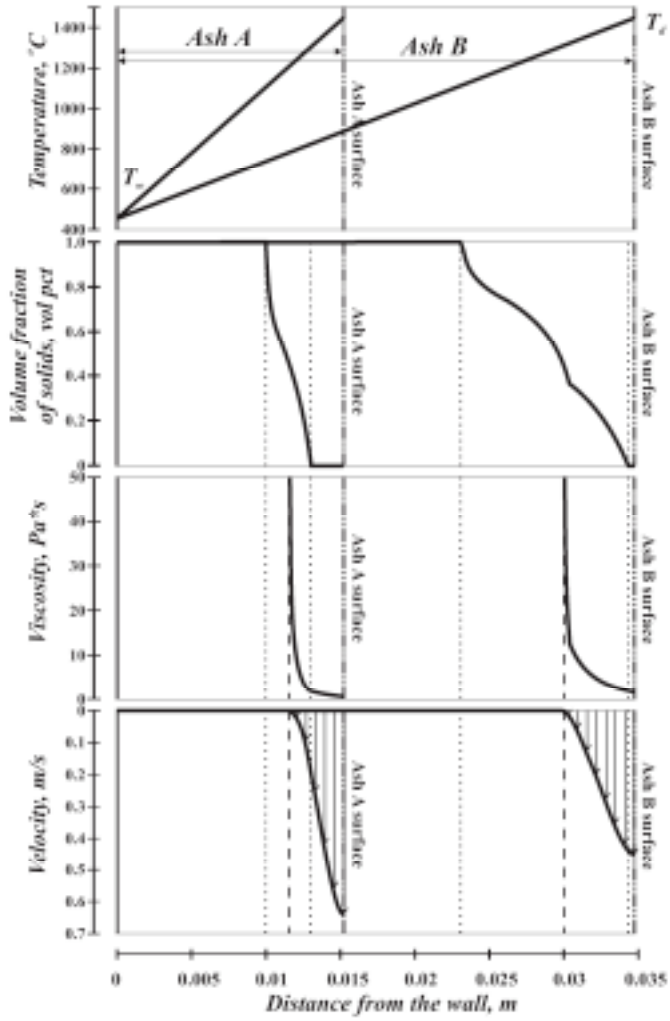

Figure 2. Temperature, proportions of solids, viscosity and slag flow velocity profiles predicted with new models for coals A and B.

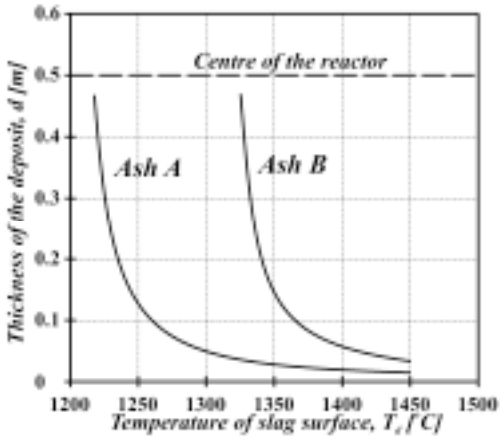

Figure 3. Thickness of the deposit as a function of temperature of the slag surface for coals A and B.

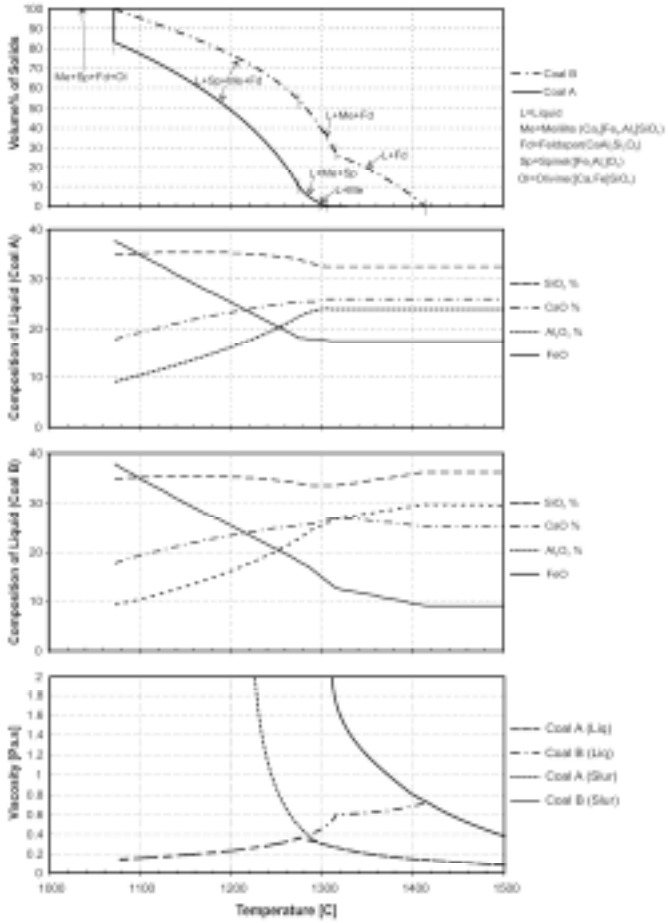

Figure 4. Crystallisation characteristics and viscosities of the coals A and B at metallic iron saturation as a function of temperature.

Conclusions

Using new chemical thermodynamic and viscosity models it is now possible to predict the behaviour of complex slag systems relevant to coal utilisation technologies. Properties such as phase equilibria, liquidus temperatures and viscosities of single and multiphase slags can be systematically analysed as functions of a given compositional variable through the selection of appropriate sections in compositional space. This has been illustrated with examples for the system FeO-Fe_2O_3-CaO-SiO_2-Al_2O_3 for a range of compositions and temperatures relevant to entrained coal gasification technologies. Effects of MgO, Na_2O and K_2O on phase equilibria can also be now predicted.

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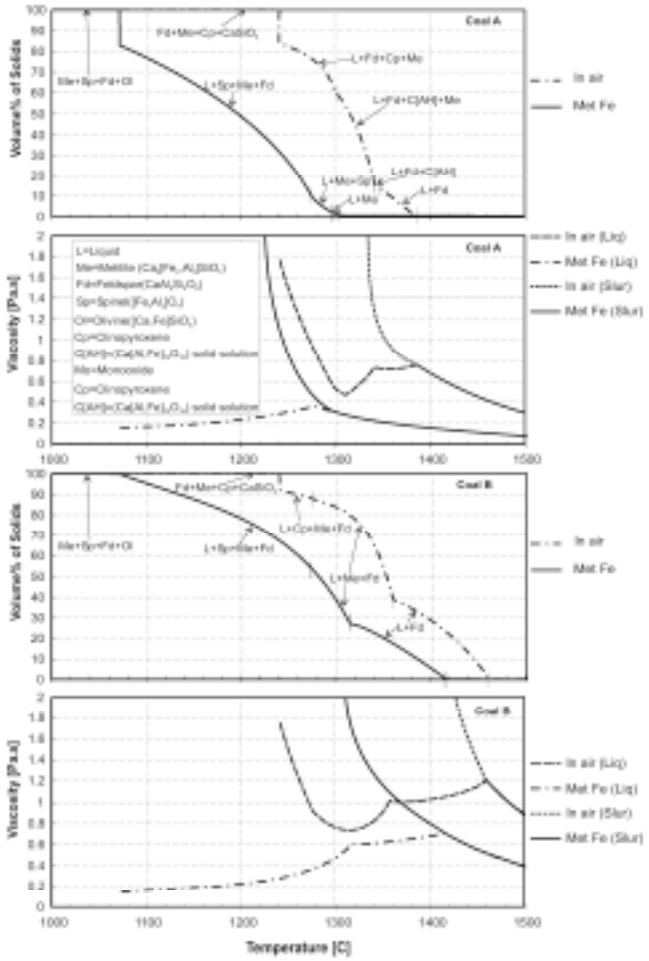

Figure 5. Effect of atmosphere conditions on crystallisation characteristics and viscosities of the coals A and B (at metallic iron saturation compared to air) as a function of temperature.

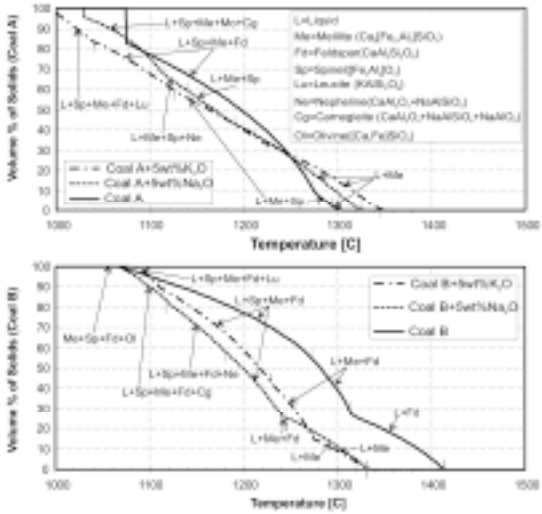

Figure 6. Effect of Na2O and K2O on crystallisation behaviour of the coals A and B at metallic iron saturation as a function of temperature.

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