

PREDICTION OF SLAG FORMATION DURING COAL COMBUSTION USING FACTSAGE EQUILIBRIUM MODELLING

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Abstract

In this paper, a thermo-dynamic model (based on FACTSage) has been used to predict the slag behaviour of coals under the high temperature conditions existing in the pf boilers. The viscosity of the slags has been calculated based on the amount and composition of the predicted molten phase and compared with the experimental data derived from entrained flow reactor (EFR). The nature of the deposits collected varies from completely molten, strong to weak deposit depending on the probe location in the EFR. The results of the slag viscosities obtained at specific temperatures between 1300 °C and 1250 °C fall within the region that corresponds to the probe 2 where sintered deposits were collected from the EFR. The Factsage calculation also revealed that this region corresponds to the region where the percentage of iron and calcium in the slag liquid reached its peak. The results revealed that the abundance of melted ash particles are dominant factors can be used to assess the strength of deposits.

Keywords: Coal; EFR; FactSage; Viscosity; Slag

Introduction

The coal ash contains significant proportion of mineral and inorganic components that lead to slagging and fouling deposits in boilers. Uncontrolled and/or unexpected formation of ash deposits on the heat transfer surfaces in a boiler can interfere with operation and reduce output or efficiency. With reduces furnace heat absorption capacity, increase furnace temperature elsewhere where may cause intensive slagging. These factors affect the overall performance of the plant including electricity production capability, equipment failure rate and hence the power generation cost (Wigley & Williamson, 1998).

Slagging refers to ash deposition in the furnace region of the boiler where heat transferred is exposed to radiant heat. The ash deposit is commonly molten and composed of highly fused particles. Another form of slagging is sintered deposit which is composed of partially fused particles. Slag may be homogenous or heterogeneous depending on factors such as the concentrations of dissolved inorganic elements, the rate of crystallization of inorganic species and the cooling rate of the liquid (Kondratiev and Jak, 2001). In a coal-fired power station, the sintered deposits can become very hard and difficult to remove by sootblowing. The strength of the deposit may be more important than the rate of deposition to an operator. The degree of sintering and hence the strength of the deposit is dependent on the chemical and mineralogical composition of the fly ash particles, the particle temperature, the surface temperature of the deposit and the gas temperature. The most widely used methods for characterizing coal ash deposition and slagging are ash fusion temperature (AFT), ash particle viscosity and ash chemistry (McLennen, Bryant, W. Bailey, Stanmore & Wall, 2000). The AFT, which determines the temperature at which the various stages of the ash deformation and flow takes place, is based on the judgment of the analyst as to when the ash reaches and passes through the

defined stages of the deformation. Since the assessment of this method is considered more empirical and subjective in nature and the results obtained may be unreliable.

The abundance of slag-liquid and viscosity of the slag-liquid are the key components requires for the deposit growth and sintering (Raask, 1985). The stickiness of liquid phase has been quantified, as suggested by many publications on the mathematical modelling of slagging. When the temperature of the particle is higher than the softening temperature the particle will sticks to the heat transfer surface otherwise it is rebounded (Mao, Kuhn & Tran, 1997). On this basis another concept of sticking probability was developed based on the melting curve of alkali-rich and silica-rich particles. In the work of Kaer et al. (Kaer, 2001), it has been assumed that the mass of the molten phase is non-sticky if the mass of the molten phase is below 15 %. Between 15 and 70 %, the mass of the molten phase is assumed to be sticky. Above this percentage, the mass of the molten phase is assumed to be flowing.

Although sintering processes can occur by vapour transport, surface diffusion, volume diffusion and viscous flow (Watt, 1969), the mechanism of viscous flow sintering appears to be the dominant mechanism responsible in creating silicate-based melts in the ash (Plaza, Ferens, Griffiths, Syred & W, 2003). The viscosity of liquid phase present in ash deposit is inversely proportional to the rate of sintering them and will decrease rapidly at elevated temperature. In the work of Raask et al. (1985) viscosities in the range of 10^7 - 10^{11} Pa*s resulted in the formation of significant sintered deposits in coal-fired boilers. A high viscosity implies a weak deposit where initial deposits are formed on clean boiler tube and the degree of sintering is low. With increasing temperature of the outer deposit surface, the ash viscosity decreases (more liquid) and sintering process become more important. The rate of the process increases with the temperature and the molten liquid (highly viscous) may eventually run down the deposition probe surface. Therefore, the developments of deposit strength depend on different temperature regimes as listed in Table 1.

Table 1: Viscosity scale for typical bituminous coal ash (Raask, 1985)

Event	Viscosity range (log ₁₀ Pa *s)	Temperature (°C)
Onset of sintering	9-11	930-1030
Medium-rate sintering	7-9	1030-1130
Rapid sintering	5-7	1130-1280
Formation of nonflowing slag	3-5	1280-1380
Slag flow due to gravity	2-5	1380-1430
Slag flow	0-2	>1430

Numerical prediction of ash deposition is used to advance the understanding of the underlying processes that lead to deposit formation, and it is considered as a powerful tool for the design and optimization of the operating parameters. Several attempts have been made to accurately predict the slagging behaviour of solid fuels in boiler situations. Slagging and fouling indices derived from the ash composition are simple models used to predict the ash behaviour in advance before the actual plant operation. The most commonly applied index is the basic-to-acid (B/A) ratio. Increasing the B/A of the coal decreases its fusibility and hence increases the slagging potential. Coals having $B/A \geq 0.11$ are considered as bad coals (Lawrence, Kumar, Nandakumar & Narayanan, 2008). There are many similar indices to describe ash behaviour. However, it is difficult to extrapolate a specific value from one type of coal to another type of

coal, since slagging is also high dependent on the fuel type, local conditions, boiler geometry and operating conditions.

The second class of models used to assess the melting behaviour of coal ash slag are thermodynamic calculations. The most popular models of ash deposition are CFD-based models which combine deposition models with the complex flow patterns of a typical boiler. A two-dimensional model by Huang et al. (Huang, Norman, Pourkashanian & Williams, 1996) related to a deposition model to boiler condition in a pulverized coal combustor. The model assumption is that an impact involving any viscosity below a critical value results in the particle sticking. For viscosities lower than the critical viscosity, the sticking probability equals unity. Obviously, the choice of critical viscosity greatly affects the sticking probability of any particles on the deposition surfaces. The value of critical viscosity has been a topic of much discussion and various workers have proposed different value to describe the results obtained from experimental investigations. While Walsh et al. (Walsh, Sayre, Loehden, Monroe, Beer & Sarofim, 1990) used a value of 10^8 Pa-s, Srinivasachar et al. (1990) suggested that the critical viscosity is between 10^4 and 10^8 Pa-s for that for some US bituminous coals. Although the CFD-based models of ash deposition provide detailed local analysis of the flow, it has not been proven to be very successful in chemical thermodynamic calculation of oxide systems (commonly referred to as slags) which is significant in coal combustion.

In the last decade, an improvement in computational methods has made it possible to perform chemical thermodynamic calculations of oxide systems. One of the predictive tools used successfully in chemical thermodynamic model of oxide systems is the computer package FactSage™ (Bale, 2009). 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 coal ash slag systems.

Since a good theoretical estimation of melting behaviour would require use of multiphase, multicomponent equilibrium calculations. In this paper a thermo-equilibrium calculation for a combustion process is applied to develop reliable models for predicting melting behaviour of slags which will then allow the assessment strength of deposits. The aim of this paper is to predict the viscosity of the actual slag by combining viscosity model with the equilibrium calculation. The organisation of the paper follows. Section 3 described the experimental investigation from the Imperial College EFR for the ash deposition and sintering of the coal combustion (Huang, Norman, Pourkashanian & Williams, 1996). In section 4, the results of the model predictions are presented and discussed together with relevant experimental data.

Methodology

In order to investigate ash sintering tendency, the following prediction methods have been used in this study: (i) thermodynamic equilibrium calculations, (ii) viscosity calculations. Fact Sage 6.2 (Bale, 2009) for the prediction of chemical equilibria through Gibbs energy minimization is a powerful tools in studying the chemistry of processes involving all molten salts, oxides, aqueous solutions, and gases. FactSage™ was introduced in 2001 and is the combination of FactWin and ChemSage-two well-known models in the area of computational thermochemistry. The software packages consist of a series of database and manipulation modules that enable the users to perform a wide variety of thermochemical calculations, including those of multiphase computations.

When the elementary compositions of the fuel and air, pressure and temperature have been introduced and a slag type is selected from the default list of slags, FactSage will search the thermodynamic database for the species including all the elements in the slag type selected. It is thus possible to determine the quantity as well as quality of the gas phase, liquid phase and solid phase. In this investigation, FactSlage A-type is selected (containing 1144 species - 278 gas, 173 liquid, and 693 solid species). These species include the elements C, H, O, N, S, Cl, Si, P, Ca, K, Na, Mg, Al, Fe, Ti, and Mn. The physical and chemical properties of coal and biomass composition are presented in Table 1. The temperature range considered was from 1200–1600 °C with a step of 100 °C. 1000 kg fuel is used as a basis for the equilibrium calculation. The FactSage database contains more than 300 gaseous, liquid, and solid phases, including salt melt and mineral melt; however, this investigation only looked at the slag liquid, slag liquid composition and solid phase that are stable at the designated temperature range.

The slag-liquid comprises SiO_2 , Al_2O_3 , FeO , CaO , K_2O , Na_2O , MgO , MnO and TiO while the solid phase includes mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}(\text{s})$), tridymite ($\text{SiO}_2(\text{s})$), leucite ($\text{KAlSi}_2\text{O}_6(\text{s})$), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}(\text{s})$), hematite ($\text{Fe}_2\text{O}_3(\text{s})$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8(\text{s})$), forsterite ($\text{Mg}_2\text{SiO}_4(\text{s})$) and spinel ($\text{MgAl}_2\text{O}_4(\text{s})$). This type of calculation has some limitations. The equilibrium calculations are based on the assumptions that all reactant are well mixed (homogeneous) and kinetic limitations are not taken into account. It must be stressed that FactSage only predict evaporative transport routes for the element and species, and do not take into consideration of the effects of particle entrainment, which are significant in combustion (van Dyk, Waanders, Benson, Laumb & Hack, 2009).

Source of Experimental data

The Entrained Flow Reactor (EFR) was designed to closely simulate the conditions which pulverize and ash particles experience in large-scale furnace (see Figure 1). The measurement techniques employed and the data obtained were reported in (Manton, Williamson and Riley, 1997; Wigley, Williamson, Malmgren and Riley, 2007) and these are summarized as follows. The reactor consists of four independently electrically heated furnaces, approximately 5 m long vertical tube with a diameter 100 mm. These furnaces provide a temperature gradient from 1650 °C at the top to 1200 °C at the bottom. A series of joints between each furnace accommodates the probes which allows the ash and char particles to be withdrawn from the combustion atmosphere. The gas temperatures at the ports 1, 2 and 3 are approximately 1400 °C and 1200 °C, respectively. Uncooled ceramic probes have been used to collect the ash deposits. The burner section consists of the primary inlet through which the primary air and the pulverized coal are fed, and the secondary air inlet, for the hot swirling air.

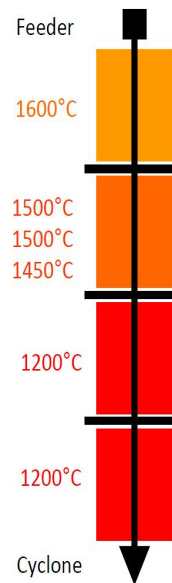


Figure 1: Schematic diagram of the Imperial College EFR (Wigley, Williamson, Malmgren & Riley, 20007)

Two typical bituminous UK power station coals (Russian and South African) were chosen as they are similar in composition, but behave differently when fired in an EFR, see Table 2. The fuel samples studied were dried, milled and sieved so that their diameters were less than 100 μm . The samples were then blended and dried at 120 °C in nitrogen gas prior to use. 100 g of fuel mixture was run for duration of 30 min, and the deposit sample was collected on probe 2 which is located in the midsection of the EFR. The probe has thermocouples that register the surface temperature of the deposits.

The ash deposits collected on the probes were then coated in a low viscosity epoxy resin, which penetrates the open porosity of the sample, and this gives stability to the deposits. Sections through the deposits were then cut to reveal a cross section. Two cross-sections were mounted in resin blocks and the samples were ground and polished for sintering analysis in a Scanning Electron Microscope (SEM). The cross-section through ash deposit containing the sinter ash and crystalline materials is shown in Figure 2.

The deposits collected at probe 1 (1500°C) were all of highly fused nature, with the most fused deposits flowing around the probe while the deposits collected at probe 1 (1200°C) were of lightly sintered nature, with distinctively visual differences in the degree of fusion. The ash deposits collected on the probes 1 and 2 were then coated in a low viscosity epoxy resin, which penetrates the open porosity of the sample, and this gives stability to the deposits. Sections through the deposits were then cut to reveal a cross section. Two cross-sections were mounted in resin blocks and the samples were ground and polished for sintering analysis in a Scanning Electron Microscope (SEM). The microstructures of the deposit from different deposition probes were compared (Wigley & Williamson, 1998).

Table 2: Coal and biomass ash content (wt %) and chemical composition (wt %) (Wigley, Williamson, Malmgren and Riley, 2007; Phyllis, 2004)

Component	R. coal	S. coal		R. coal	S. coal
Proximate analysis	Wt % on dry basis		Ash composition	Wt % on dry basis	
Volatiles	30	Al ₂ O ₃	SiO ₂	60.1	54.1
Fixed carbon	76	Fe ₂ O ₃	Al ₂ O ₃	24.0	33.5
Moisture	5.56	CaO	Fe ₂ O ₃	6.0	3.1
Ash	12.6	MgO	CaO	4.1	4.1
CV(MJ/kg)	27	K ₂ O	MgO	1.1	1.3
Ultimate analysis	Wt % on dry basis		K ₂ O	3.0	0.7
C	76.5	TiO ₂	Na ₂ O	0.4	0.1
H	4.5	MnO	TiO ₂	1.2	1.7
O	4.9	P ₂ O ₅	MnO	0.1	0.0
N	1.9	1.78	P ₂ O ₅	0.0	1.4
S	0.4	0.83			
Cl	0.25	0.00			

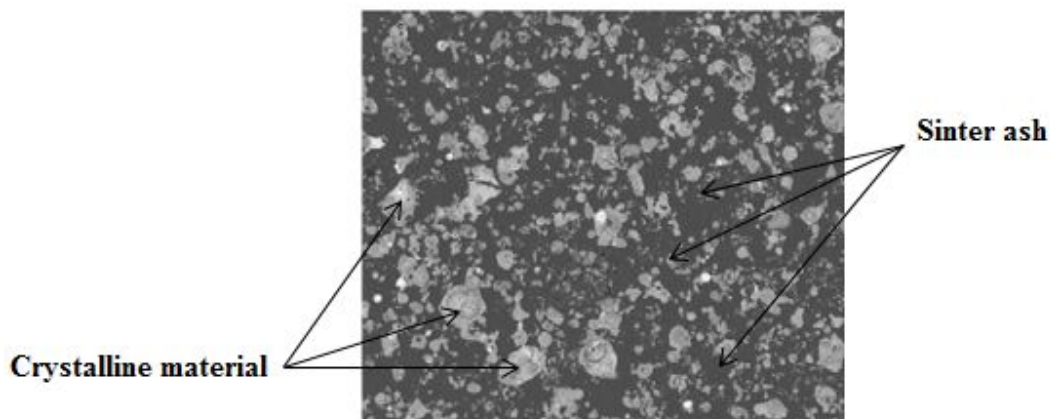


Figure 2: Cross-section through ash deposit containing the sinter ash and crystalline materials (Wigley, Williamson, Malmgren & Riley, 2007)

Results and Discussion

Substantial liquid formation requires higher temperatures: for the South Africa and the Russian coals shown in Figure 3, approximately 60% liquid is predicted at 1500 °C. Also, the extent of liquid formation depends on the fuel ash. The larger amount of slag liquid for the Russian coal in the temperature range of 1300 to 1600 °C may be attributed to the high Fe₂O₃ content which is greater than the sum of CaO and MgO in the fuel ash. Conversely, the low slag liquid predicted in Figure 3 is due to the fact that Fe₂O₃ content in South Africa coal is less than the sum of CaO and MgO in the fuel ash. The slag obtained depends on the gas temperature at the sampling port of EFR as this will directly affect the degree of assimilation of the iron phases into the aluminosilicate melt. Previous research, such as McLennen et al. (McLennen, Bryant, Bailey, Stanmore and Wall, 2000) has shown that the higher content of divalent iron in reduced conditions promote the formation of the molten phase.

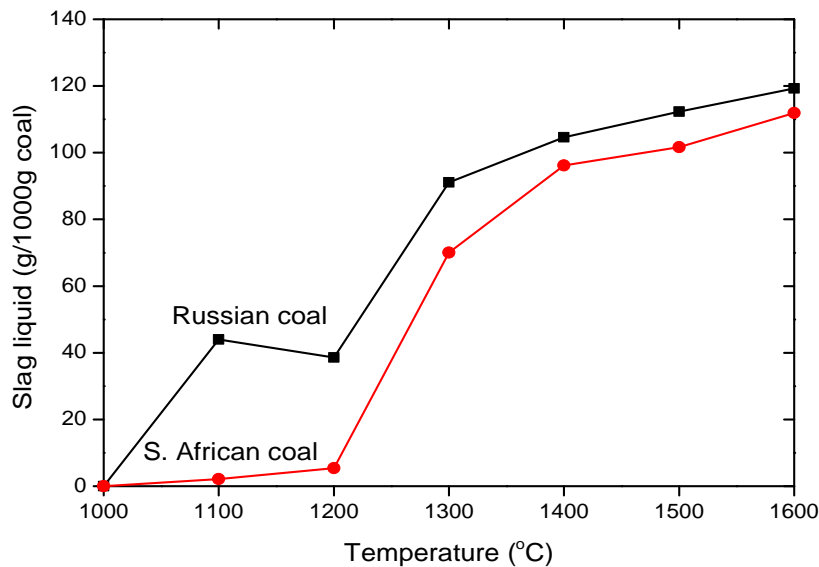


Figure 3: Mineral matter output from the Russian and South African coal combustion at different temperatures

The FactSage results show that mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) is the main solid phase in South Africa coal as shown Figure 4, and this persists at 1600 °C. In contrast, the main solid in the Russian coal ash is tridymite (SiO_2), see Figure 5. From the ash content and chemical composition of the coals in Table 1, it is observed that Russian coal has high SiO_2 (60.1 wt.%) and low Al_2O_3 (24 wt.%) while South Africa coal has SiO_2 (54.1 wt.%) and high Al_2O_3 (33.5 wt.%) in the ash. The difference in the identity of the primary solid phase results from the differences in the composition of the ash: higher SiO_2 in the fuel ash favours tridymite formation, while higher Al_2O_3 levels favour mullite formation. Leucite (KAlSi_2O_6), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) are formed because of the interaction between of quartz with Al_2O_3 and CaO at about 1000 °C. Hematite (Fe_2O_3) and leucite (KAlSi_2O_6) appear at about 1400 °C but leucite (KAlSi_2O_6) which has a significant effect on the fusion characteristics rises sharply and remain fairly constant at 1230 °C. The slag disappears at 1000 °C for both the South Africa and Russian coals. In Russian coal, potassium silicate is characterized by large variations probably due to the periodic formation and dissolution of crystals in the melt (see Figure 5). The high amount of calcium, iron and potassium lead to the formation of Ca-, K- and Fe- silicates that are crystallized even at 1500 °C. This may simplify the operation of the EFR because the ash will be relatively non-sticky.

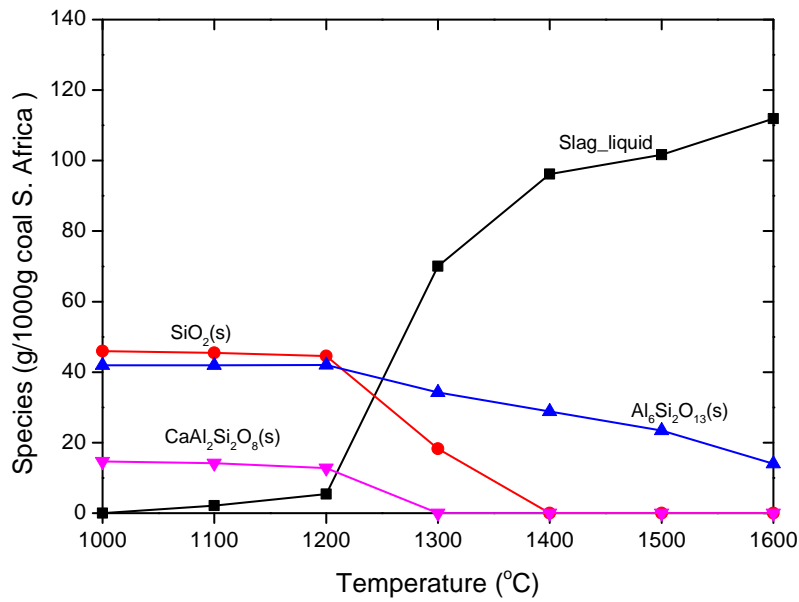


Figure 4: Mineral matter output from the South African coal combustion at different temperatures

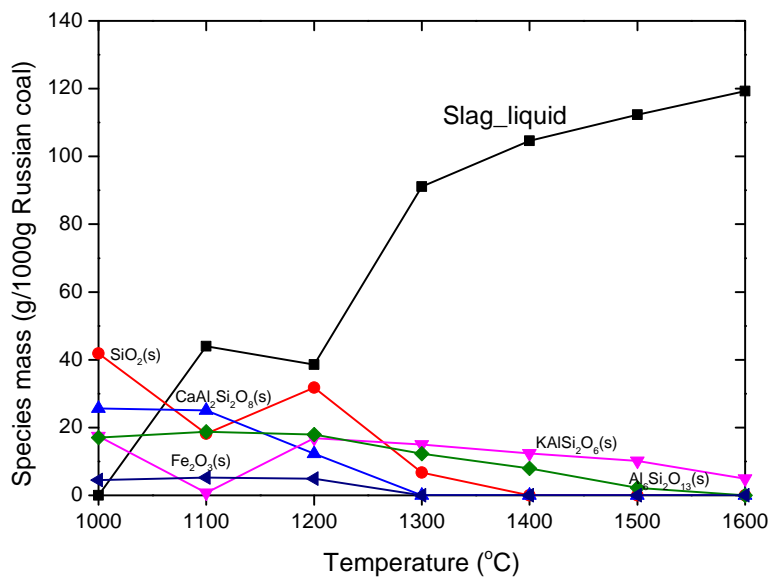


Figure 5: Mineral matter output from the Russian coal combustion at different temperatures

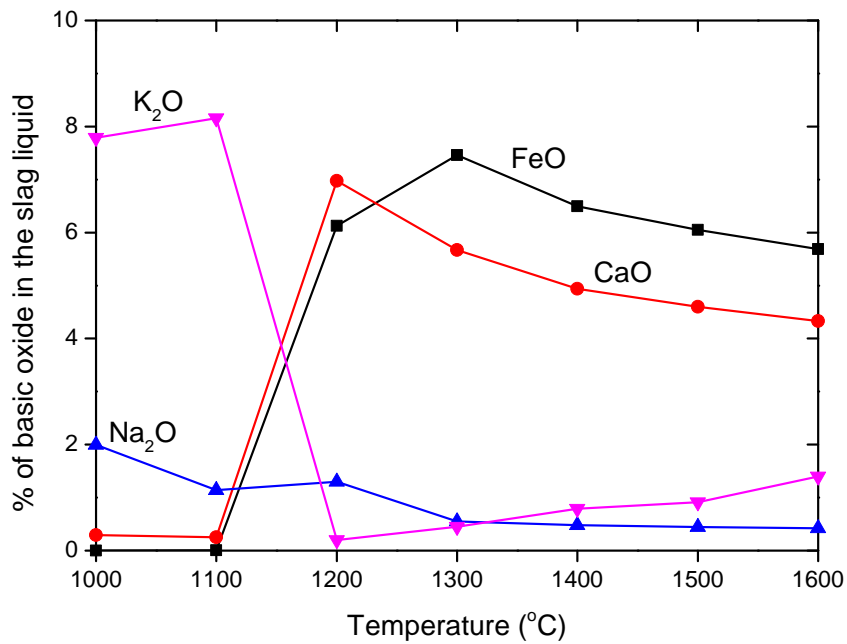


Figure 6: % of basic oxide in the slag liquid for Russian coal combustion at different temperature

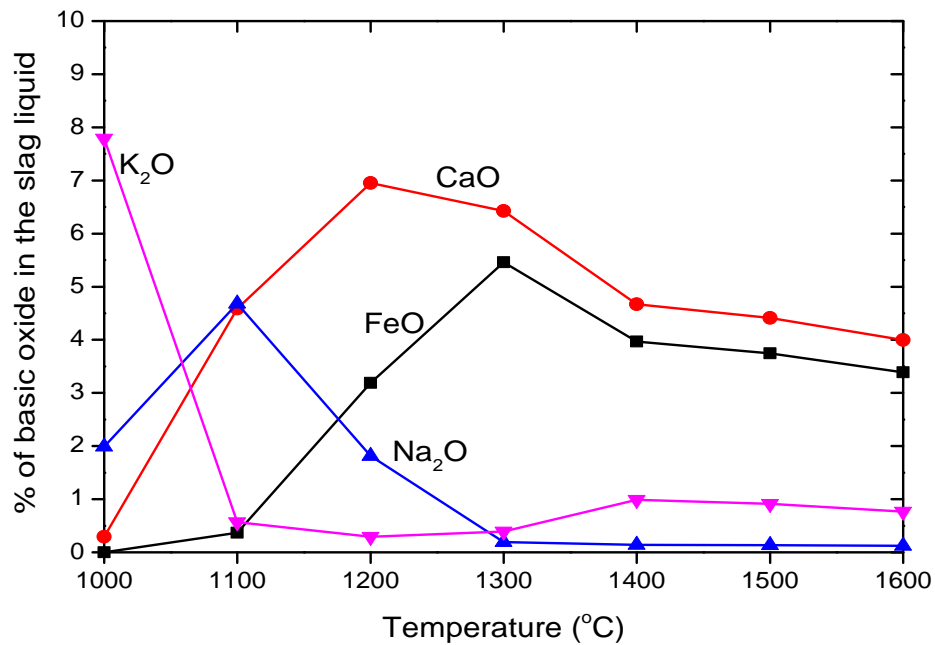


Figure 7: % of basic oxide in the slag liquid for South African coal combustion at different temperature

It can be observed from the results presented in Figures 4 and 5 that mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and tridymite (SiO_2) are higher in Russian coal in comparison with South African coal and this has been reported (Oh, Brookerb, de Pazb, Brady and Deckerb, 1995) to increase the particle-to-particle bonding and act as a strong bridge between these particles. As the concentrations of oxide in the slag increase, the solubility limit is reached and metallic oxide will form solid from the slag as shown in Figures 4 and 5. Alternatively, unassimilated oxides may simply occur as crystalline within the glass matrix if either of these processes occur, the presence of crystalline phases will increase the viscosity and inhibit sintering. Figure 6 and 7 show the percentage of basic oxides in the slag liquid for Russian coal and South Africa coal respectively. The percentage of iron and calcium increased significantly when the combustion temperature is in excess of $1100\text{ }^\circ\text{C}$ while potassium and sodium increased when the combustion temperature is less than $1100\text{ }^\circ\text{C}$. As the iron and calcium concentration of aluminosilicate glass increases, up to a certain level, the viscosity will tend to decrease and the rate of deposit sintering is enhanced. However, at higher concentration of oxides in the slag, the solubility limit of such oxide is reached and oxide crystallised out in form of mullite, tridymite, leucite, cordierite, hematite, anorthite, forsterite and spinel (see Figure 6 and 7).

Conclusion

The nature of the deposits collected varies from completely molten, strong to weak deposit depending on the probe location in the EFR. The results of the slag viscosities obtained at specific temperatures between $1300\text{ }^\circ\text{C}$ and $1250\text{ }^\circ\text{C}$ fall within the region that corresponds to the probe 2 where sintered deposits were collected from the EFR. The Factsage calculation also revealed that this region corresponds to the region where the percentage of iron and calcium in the slag liquid reached its peak. Moderate temperature ash deposits are most prevalent when iron and other fluxing agents are present in the ashes. In order for ash particle to become sintered, it must be sticky enough to stay in place on vertical surfaces, then harden sufficiently as the deposit grows to prevent shedding, erosion, or breakage from gas pressure and particle erosion. The model successfully predicts the viscosity of the slag and trend of decreasing in viscosity with increasing slag formation.

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