

Thermodynamic Modelling of Effect of Flux on the Liquidus Temperatures and Phase transitions in Coal Ash

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ABSTRACT

Plant shutdowns due to the accumulation of ash materials in the boilers is a commonly practiced problem in thermal power sectors. Cleaning of ash products at regular intervals need to be necessary for maintaining the good furnace operation conditions. Use of slagging technology is the best practice for the removal of high temperature ash products, in which the melting temperature of ash is lowered by using the additive technology. In this paper, the properties of ash products formed during the combustion of low grade Indian coal were analyzed in terms of proximate and ash fusion temperature analysis. The effect of flux addition on the slagging behavior of Indian coal ash was analyzed. The AFT analysis of Indian origin coal ash shows that it is of non-fusible type. The formation of high temperature stable phases like kaolinite and quartz are the reason for high AFT temperatures in Indian origin coal.

INTRODUCTION

Since centuries coal is the main fuel resource for the power generation sectors. Over fifty percent of power generation is produced through coal fired thermal power plants. Unfortunately, there is degradation of coal quality as the high quality natural coal resources are degrading at very rapid rate. While, the use of low quality high ash coals affects the furnace operation efficiency due to the deposition of ash. Removal of these ash products from the boilers in regular intervals is necessary to maintain the efficiency of furnace operation. Soot blowing is widely used for the cleaning of ash deposits in thermal power plants and gasifiers. In soot blowing, high speed water jets are used to blow up the ash deposited in furnace tubes. But, the clinkers and partially melted slag deposits are very difficult to get rid of through soot blowing technique. To overcome these problems, many boilers in thermal power plants operation is modified into 'Slag Tapping' or 'Wet Bottom' types, in which the liquid ash or slag tapped continuously accumulated at the bottom of the furnace. The operation of these type of boilers is limited to the use of coals which possess an ash slag having low ash fusion temperatures (AFT), low viscosity and good flow characteristics (Shepard et al. 2002; Johnson et al. 2018). Ash slagging characteristics are mainly dependent upon the chemical composition of ash. There are numerous investigations done on the ash melting characteristics based on the initial composition of slag. Han et al. (2019) worked on the effect of high silicon rich bio-mass to the coal and noted that slagging tendency of coal ash reduces drastically with the addition of silicon-rich biomass. Huang et al. (2013) reviewed that high AFT temperatures in the coal ashes with high silica and alumina is due to the formation of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) or kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$) phase. They also noted that the addition of lime or basic compounds to these type of coal ashes lower the AFT temperatures. Lin et al. (2019) studied on the synergetic effect of calcium and aluminum additives on AFT temperatures of coal ash,

and found that Al addition increased the AFT temperatures, while AFT temperatures were lowered with CaO addition. Proper tapping temperatures and fluidity have to be maintained to obtain a continuous flow of slag to the bottom of the furnace, and inadequate tapping temperatures lead to solidification of slag which intern form as solids or sinter in the boilers. Although AFT test provides critical information regarding the slagging and fouling characteristics of coal, still it displays an error in the reproducibility by $\pm 20^\circ\text{C}$ - 100°C . It does not give any proper information about variation in the fusion temperatures based on the chemical compositions. Numerous attempts were made to find out the effect of AFTs, chemical and mineralogical composition of ash by many researchers (Chakravarty et al. 2015; Singh et al. 2015; Banerjee et al. 2016; Neupane et al. 2017; Bilen, Mehmet 2019). Several investigations were reported on the understanding of relationship between the AFT and the equilibrium phases of coal ash slags by using the thermodynamic calculations based on CALPHAD method. He et al. (2019) studied on the mechanism of ash slagging in high iron oxide coal ashes using thermodynamic calculations and experimental details, and noted that AFT of ash decreased drastically with increase in iron oxide content. They also observed that formation low temperature fayalite (Fe_2SiO_4), clinoferrosilite (FeSiO_3) and Almandite ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) phases are the reasons for lowering in melting temperature of ashes. Kong et al. (2014) observed that AFT of coal ashes lowered with the addition of CaO. They also reported that increase in conversion of high temperature stable mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) with CaO addition is the reason for decrease in AFTs of coal ashes. It is very hard to interpret the AFT of ash based on the chemical characteristics, as it is controlled by both kinetics and equilibrium phases formed. Kinetics of the process was dependent upon the mineralogy, shape, size, time and other kinetic factors, while phase equilibria can be determined by the bulk composition of coal ash. In this paper, focus on the effect of different major ash components and their interactions on the AFT results is made. The effect of calcium carbonate addition on the AFT temperature, equilibrium phase transitions, and liquid phase formation are studied. FactSage thermodynamic software based on the CALPHAD approach was used to establish the relation between AFT and equilibria phases formed during the coal slagging. FactPS and FTOxid thermodynamic databases were used for the present thermodynamic calculations.

EXPERIMENTAL WORK

Thermodynamic Calculations by Using FactSage

In present study FactSage 6.4 thermodynamic software was used to calculate the phase transitions and equilibrium products obtained by the heating of ash samples. These calculations include the changes in the liquidus temperature, solid to slag proportion with different

additives at various temperatures. The free energy of pure components was calculated by using the equation (1), and the free energy of solid solution and liquid slag phases were calculated by using the equations (2) and (3).

$$G_i^{\phi^o}(T) = a + bT + cT \ln T + dT^2 + eT^3 + FT^{-T} + gT^{-3} + hT^{-2} \quad (1)$$

$$G_i^{\phi^o}(T) = \sum_i X_i G_i^{\phi^o}(T) + RT \sum_i X_i \ln X_i + G_i^{Ex,\phi} \quad (2)$$

$$G_i^{Ex,\phi}(T) = \sum_i \sum_{j>i} X_i X_j \sum_{v=0}^{n_{ij}} L_{ij}^{\phi}(T) (X_i - X_j)^{\phi} \quad (3)$$

Where; a, b, c, d, e, f, g and h are the constants. H_i^{SS} is the molar enthalpy of the substance at 25°C and 1 bar in its standard state (ss), T is the temperature in Kelvin, L and ϕ are the Lagrange multiplier and parameter respectively.

Raw Materials

The high ash coal obtained from the Talcher coal mine in Odisha, India is used as the base raw material in this study. The calcium based flux (CaCO_3) is used as the additive for lowering the ash fusion temperature of raw coal. The CaCO_3 used in this study is of analytical grade.

Ash Fusion Temperature (AFT) Test

The ash sample required for the AFT test are prepared as given below. The raw coal or combined coal with flux was placed in an air tight muffle furnace at a temperature of 820°C for one hour. After that, the sample was taken out and air-cooled immediately. The resultant ash product was milled to 100 μm before using it for AFT analysis. The milled ash sample was shaped into a pyrometric cone with 20 mm height and 7 mm side length of a regular triangle. The pyrometric cone ash samples were placed into the AFT analyzer and closed to thermocouple (apart from 2 mm). The heating rate was controlled to 15°20°C/min under 900°C and 5 \pm 1°C/min above 900°C in a reducing atmosphere and procedure followed is according to the standard ASTM D1857 (Mishra et al. 2020; Kim et al. 2017).

Chemical Analysis and Characterization

Chemical composition of the coal ash samples was determined by using the XRF analysis (S8 TIGER). Phase analysis of the coal ash samples were conducted by using the X-ray powder diffraction analysis (Bruker D8 DISCOVER). X-pert high score software was used for the phase identification of peaks obtained from the XRD analysis.

RESULTS AND DISCUSSION

Table 1 shows the XRF results of raw coal ash and the lime added coal ash. It shows that silica, alumina, and iron oxide are the major phases present in raw coal ash. The amount of CaO is less than 1 wt.% in raw coal, and its amount increased readily with increase in the flux (CaCO_3) addition. The XRD results of the ash samples are shown in Fig.1. The mineralogical characterization of raw coal shows that quartz, kaolinite, and sillimanite are the major phases detected. The quantity of quartz and kaolinite phases decreased drastically with flux

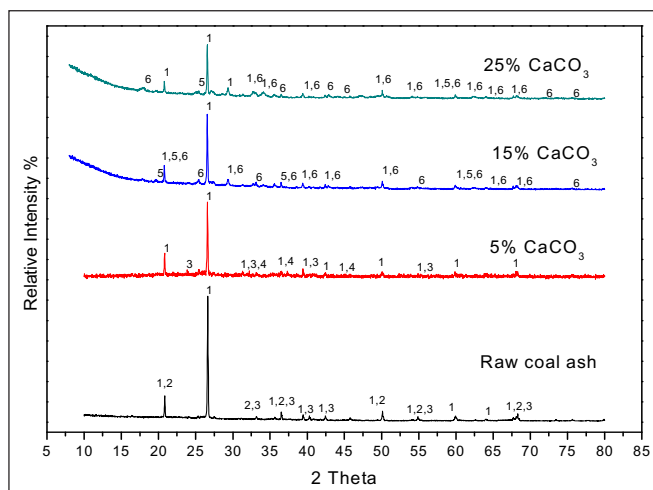


Fig.1. XPRD analysis of the raw coal ash and lime added coal ash. 1 - Quartz, 2 - Kaolinite, 3 - Sillimanite, 4 - Lime, 5 - Calcium silicate, 6 - Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)

addition, and excess calcium silicate and anorthite phase peaks are identified in the flux added ash samples.

AFT Analysis

The effect of flux (CaCO_3) amount on the fusion or melting characteristic temperatures including the deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT) of Indian coal ash are given in Table 2 and Fig. 2. It can be seen that all four characteristic temperatures drop significantly with an increase in the amount of flux. Flux addition has an adverse effect on ST and HT characteristics temperatures compared to DT and FT. Vassilev et al. (1995) differentiated coal ashes into three different categories based on the hemispherical transition temperature (HT); fusible ash which has HT in the range of 1200°C-1300°C) medium fusible ash with HT range in between 1323°C-1440°C, and refractory ash with HT greater than 1470°C. According to the present AFT analysis the raw coal ash falls under the category of refractory ash. The HT temperature of coal ash comes under 1300°C with the addition of 15 wt.% of flux, which comes under the fusible type ash. When the flux amount reached to 25 wt.% flow temperatures of coal ash dropped to below 1400°C, which is in the range of furnace operating temperature. It indicates that the required addition of flux to tap slags in boiler operating temperatures is 25 wt.%.

Thermodynamic Analysis

Thermodynamic analysis of phase transformations of ash with respect to temperature and the effect of CaCO_3 on fusion characteristics were analyzed by using the FactSage 6.4 thermodynamic software. The thermodynamic results obtained for the phase transformation occur in the coal ash with and without flux addition are shown in Figs. 4, 5, 6 and 7. In raw coal, quartz, Andalusite, leucite, and hematite phases are formed at low temperatures, with an increase in temperature

Table 1. Chemical composition of raw coal and with CaCO_3 addition

	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO%	K ₂ O%	SO ₃ %	TiO ₂ %	MgO%	P ₂ O ₅ %	Na ₂ O%
Raw Coal	65.70	23.04	5.87	0.67	1.87	0.22	1.36	0.80	0.13	0.07
CaCO ₃ (2.5%)	64.10	22.57	4.94	2.40	1.90	1.47	1.29	0.83	0.18	0.08
CaCO ₃ (5%)	62.10	22.25	4.98	4.11	1.80	2.02	1.26	0.86	0.16	0.09
CaCO ₃ (7.5%)	60.60	21.36	6.77	4.97	2.04	1.76	1.23	0.77	0.14	0.10
CaCO ₃ (15%)	47.30	24.20	5.48	15.23	1.61	1.83	1.20	2.47	0.23	0.09
CaCO ₃ (25%)	40.59	18.77	4.96	27.77	1.29	1.68	1.05	3.59	0.21	0.09

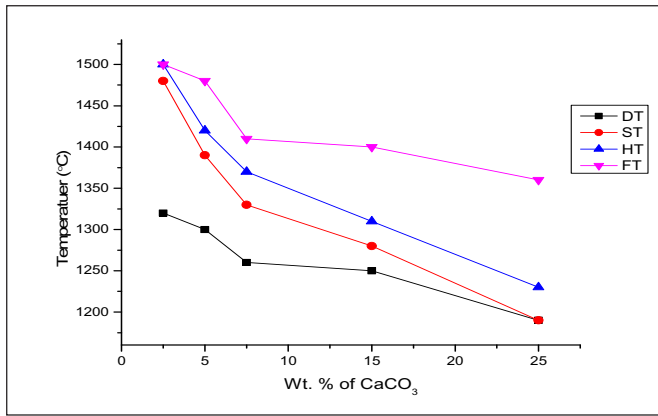


Fig.2. Effect of CaCO₃ on AFTs.

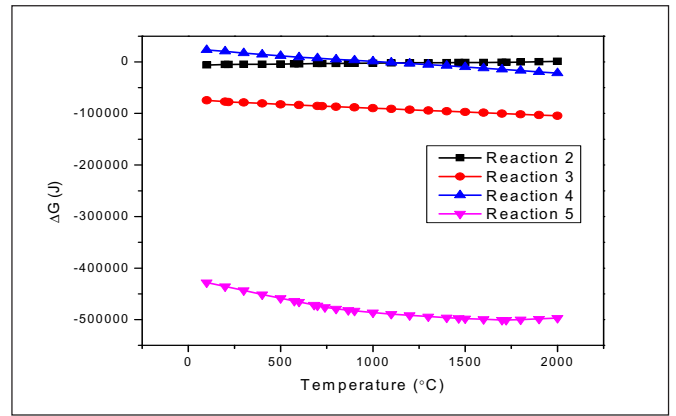


Fig.3. Gibbs free energy curve for different temperature.

tridymite, sillimanite, anorthite, Al₂Fe₂O₆ phases coexist with slag phase. High temperature stable phases tridymite and sillimanite phases are formed due to the polymorphic transition of quartz phase and

Table 2. AFT of Raw coal ash

Sample ID	DT(°C)	ST(°C)	HT(°C)	FT(°C)
Raw Coal	1350	1480	1490	1500

reaction of alumina and silica in ash. Potassium oxide, magnesium oxide, iron oxide, and calcium oxide act as major fluxing agents in the slag formation criteria of raw coal. Potassium oxide reacts with respective aluminosilicate and forms low temperature phases like leucite (KAISi₂O₆) and kaliophilite (KAISiO₄), these phases have very low melting points and they readily form slags at temperatures below

1200°C (Wang et al. 2019). Magnesium oxide forms Mg₂Al₄Si₃O₁₈ phase during the reaction with aluminosilicate. Thermodynamic observations show that Mg₂Al₄Si₃O₁₈ phase completely converted into slag at temperatures below 1400°C. CaO forms several low melting temperature ternary components like anorthite by combining with aluminosilicate (Wu et al. 2019). Even though, K₂O has higher affinity to neutralize aluminosilicate it is not used as the fluxing agent because of the volatile nature of potassium components in boiler temperatures. Hence, the calcium based compounds are most used all over the world for fluxing operation because of its abundance as lime and it does not form any re-circulatory components like potassium oxides in furnace.

Figures 4, 5, 6 and 7 shows the effect of flux (CaO) addition on the phase transition and slag formation characteristics of Indian coal.

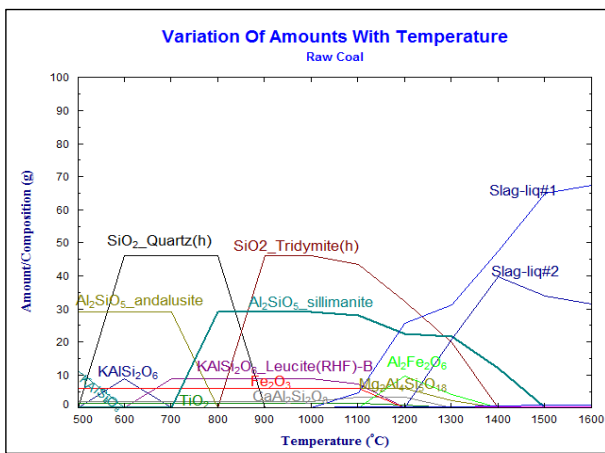


Fig.4. Phase transformation of raw coal ash

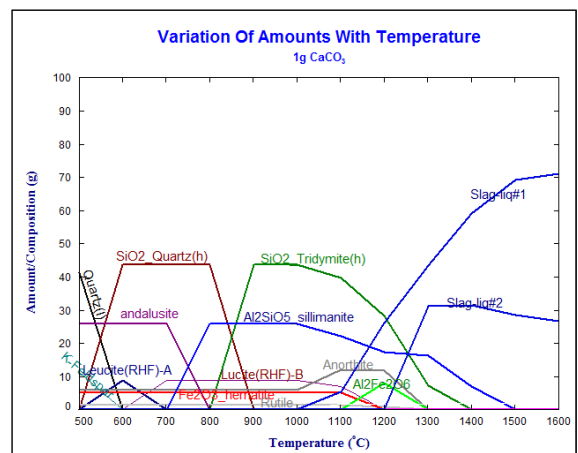


Fig.5. Phase assemblage of coal ash with mixed 5% CaCO₃ additive

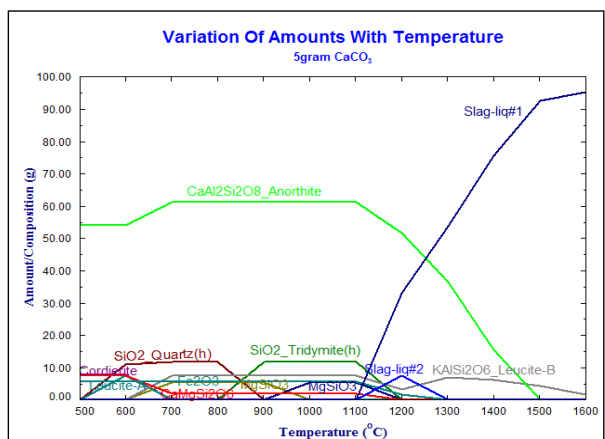


Fig.6. Phase assemblage of coal ash with mixed 15% CaCO₃ additive

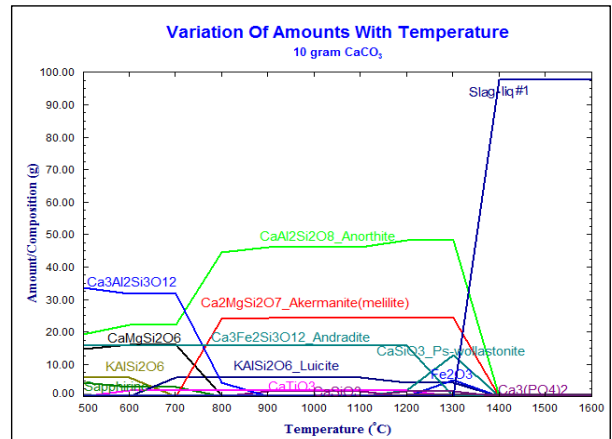


Fig.7. Phase assemblage of coal ash with mixed 25% CaCO₃ additive

The results show that at 5wt% of CaO, the last crystal phase obtained at around 1500°C is sillimanite and for 10wt% CaO, leucite phase forms even after 1600°C but in practical leucite was never observed in coal slag formation in boiler (Park and Myongsook, 2008). The second last crystalline phase anorthite was obtained at temperatures around 1500°C. The analysis for 25wt% CaO added sample did not show the leucite formation, and the last crystalline phase that was observed at temperatures below 1400°C. The experimental AFT results also show that the flow temperatures of raw were lowered to 1400°C with 25 wt% flux addition. XPRD results also show quartz, kaolinite, and anorthite phases, kaolinite phase loses water molecules at high temperatures to form sillimanite phase. The reactions that occur between the different components in the coal ash are given below:

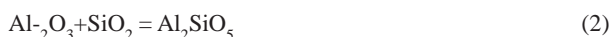
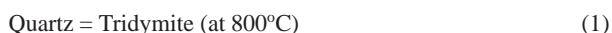


Figure 3 shows the Gibbs free energy plots for the reactions labelled in (2) to (6). It shows that, the leucite formation reaction i.e. equation 6 has minimum free energy change followed by reaction 3 at all temperatures. At temperatures below 1000°C, sillimanite formation reaction has more negative free energy compared to $\text{Al}_2\text{Fe}_2\text{O}_6$ formation reaction. Above 1000°C, $\text{Al}_2\text{Fe}_2\text{O}_6$ reaction is highly stable that means iron oxide act as a fluxing agent at high temperatures only.

CONCLUSION

High alumina and silica content in the Indian origin coal leads to the formation of stable phases like kaolinite and quartz. AFT analysis indicate that the present coal ash comes under non fusible ash type. Flux addition lowered the AFT temperatures of coal ash drastically. Advantage of lowering the AFT is that; slags formed in the boiler can be removed at lower temperatures and it is widely used in power plant industry. The main reason for the hindering in AFT temperatures with flux addition is the formation of eutectic ternary phase anorthite. The flow temperature of raw coal ash is above 1500°C. The complete molten state of ash components achieved below 1400°C with 25 wt% of flux addition (i.e. 10g CaCO_3). Thermodynamic analysis performed in present work by the CALPHAD method also supports these calculations. Equilibrium calculations of raw coals show tridymite, sillimanite, leucite and $\text{Al}_2\text{Fe}_2\text{O}_6$ are the major phases formed in the final products, all these compounds have high melting points. The addition of lime reacts with these binary compounds and form low melting points ternary compounds like Anorthite and Mullite phases which trigger in lowering AFT values.

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