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Papers in International Journals

1) Pintana, P., Tippayawong, N., “Pridiction of Slag Occurrence in a Lignite-Fired Utility Boiler,” WSEAS Transactions on Environment and Development, Vol. 10, 2014, 202-210.
2) Pintana, P., Tippayawong, N., Nuntaphun, A., Thongchiew, P., “Characterization of slag from combustion of pulverized lignite with high calcium content in utility boiler,” Energy Exploration & Exploitation, Vol. 32, No. 3, 2014, 471-482.
3) Pintana, P., Tippayawong, N., “Nonisothermal Thermogravimetric Analysis of Thai Lignite with High CaO Content,” The Scientific World Journal, Vol. 2013, Article ID 216975, 1-7.

Papers in International Conference

4) Pintana, P., Tippayawong, N., Ingham, D.B., Pourkashanian, M., Ma, L., Jones, J., Williams, A., “Assessing Potential Occurrence of Slag in Combustion of Thai Coal by Evaluation of The Ash Melting Temperature,” 13th International Conference on Clean Energy (ICCE-2014), Istanbul, Turkey, 8-12 June 2014, 117-123.
5) Pintana, P., Tippayawong, N., “Predicted formation and deposition of slag from lignite combustion on pulverized coal boilers,” 2014 International Conference on Chemical Engineering and Materials Science (CEMS’14), Venice, Italy, 15-17 March 2014, 155-159.
6) Pintana, P., Tippayawong, N., Nuntaphun, A., Thongchiew, P., “Physical Characterization of Slag from Combustion of Lignite with High Ca Content,” International Conference on Green and Sustainable Innovation 2012 (ICGSI 2012), Chiang Mai, Thailand, 24-26 May 2012, 194-201.

Prediction of Slag Occurrence in a Lignite-Fired Utility Boiler

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Abstract: - Lignite from Mae Moh mine is the largest source of solid fuel for electricity generation in Thailand. It is used in pulverized coal-fired boilers of a 2400 MW thermal power plant. Its high CaO content in ash is a major concern that can affect severe slagging. In this paper, potential of slag occurrence in the power plant was investigated by numerical simulation. The FactSage thermochemical package was used to predict ash and slag behaviour, as well as ash fusion temperature. A commercial CFD package was also employed to simulate gas velocity and temperature distribution, particle trajectory and temperature, and wall heat flux in a utility boiler of the power plant. The results were found to show good quantitatively and qualitatively prediction of slag formation. They can be applied to predict slag deposition inside the boiler effectively.

Key-Words: - slag, lignite, pulverized coal-fired boiler, coal combustion, FactSage simulation, CFD simulation

1 Introduction

Coal is one of the main natural resources that contains energetic materials for combustion. It is widely used in electricity generation [1]. Lignite is typically brown, soft, and friable, containing high moisture, low carbon, hence low energy density. Higher rank coals (bituminous and anthracite) are generally black, hard, and strong, having low moisture, high carbon, high energy content, and often used in cement and steel industries [2].

In Thailand, about 17 million tons of the lignite from Mae Moh mine was used annually for Mae Moh power plant under management of Electricity Generating Authority of Thailand (EGAT). The Mae Moh plant consists of 10 pulverized coal-fired boilers with a total capacity of 2,400 MW, accounting for about 12% of the national electricity consumption. The lignite is usually of poor quality and has different properties at various mining areas. The lignite is usually blended to meet the power plant requirement [3]. However, the recent survey of remaining lignite showed that they are of lower quality. High CaO in ash of the lignite is that main issue that can affect severe slag in future operation of the boilers. It is a major challenge faced by EGAT engineers [4].

Slag is waste products from lignite incineration. Main products are fly ash and bottom ash [5]. Slag is caused by many factors, such as the coal organic properties, coal mineral matter properties, mineral transformation and decomposition, temperature of the boiler furnace, the fluid dynamic, ash transport, vaporization and condensation of the ash species, deposit chemistry-specie migration and reaction etc. [6-7]. Slag consists of fused deposits or a re-solidfied molten material that forms primarily on the walls of the furnace or on other surfaces predominately exposed to the radiant heat or excessively high gas temperature [8]. When the slag occurs, the soot blowers are normally put in operation to remove it from the wall. However, if slag in the boiler becomes excessive, the soot blowers may not be able to handle it. The built-up slag will bring about a loss in radiation heat transfer, leading to lower overall boiler efficiency. Subsequent problems associated with slag such as loss of heat, loss of capacity, boiler equipment damage, loss of time and money in maintenance boiler will also occur.

Although EGAT attempted to solve the slag problem, but it seemed that so far there was no good practical solution. Potential of slag (combined effect of the slag liquid formation, ash flow distribution, and temperature profiles) in a pulverized coal-fired boiler remains to be a great interest.

2 Methodology

The properties of Mae Moh lignite were analyzed for proximate and ultimate composition, as well as its heating value. Results are shown in Table 1 [9]. Additionally, its ash composition and ash fusibility temperatures (AFT) were analyzed and the results are shown in Table 2 [10-15]. These properties were prepared for use in the software programs.

Table 1 Lignite properties

Proximate analysis (%w/w, as-received basis)	
Moisture content	35.07
Volatile matter	28.17
Fixed carbon	25.86
Ash	10.91
Ultimate analysis (%w/w, dry basis)	
Carbon	58.54
Hydrogen	3.00
Nitrogen	1.89
Oxygen	12.88
Sulfur	5.49
Heating value (MJ/kg dry basis)	
HHV	22.80
LHV	22.15

Table 2 Ash properties

Ash composition (%w/w)	
SiO_2	21.28
Al_2O_3	13.43
TiO_2	0.24
CaO	11.08
Fe_2O_3	28.03
Na_2O	1.87
MgO	4.02
K_2O	1.31
SO_3	18.64
P_2O_5	0.07
MnO_2	0.04
Ash fusion temperature (°C)	
IT	1235
ST	1305
HT	1340
FT	1480

2.1 Ash Melting Point Prediction

The FACTSAGE program has been developed as an efficient predictive tool prediction of liquidus temperature, proportions of solids, mineral formation, and phase equilibria of ash samples [11-18]. FactSage is the fusion of two well-known software F*A*C*T/FACT-Win and ChemSage and it is the largest thermochemical package and database available for inorganic solid and slag in the field of computational thermochemistry. The package runs on a PC operating under Microsoft Windows [10].

The Equilib module (thermodynamic application calculations) and Phase Diagram module (phase diagram calculations) are used to incorporate the FactSage Gibbs energy minimize [19]. It calculates the concentrations of chemical species when specific elements or compounds reacted or partially reacted, in order to reach a state of chemical equilibrium [20]. In this study, these modules (supported by ETII, the University of Leeds) were used to predict the ash behaviour and the ash fusion temperature.

2.2 CFD Simulation

Computational fluid dynamics (CFD) has been used to simulate the firing of coal combustion under different operating conditions extensively [21-26]. In this work, a commercial CFD package, ANSYS FLUENT, was used to predict gas flow, temperature distribution and particle trajectory that can adapt to predict slagging behavior [21-25, 27].

In general, coal combustion in CFD models is used to solve for fluid flow, turbulence, particle trajectory, heat transfer, chemical reactions of the fuel, and the formation of pollutants [28]. In this study, FLUENT version 13.0 was used to predict the temperature and flow distribution inside a boiler. The wall heat flux was evaluated for comparison with real operating parameters. The information was combined with those from the previous FactSage method to predict deposition of slag in the boiler furnace. All numerical simulation was performed at ETII, the University of Leeds.

A Mae Moh boiler is of 300 MWe capacity and tangentially fired type. The geometry is shown in Fig. 1. The dimensions are 13.8 m in width and 15.3 m in depth. The height from the lowest at hopper to the highest point at superheater and reheater is 54.3 m. On the walls, there are four windboxes for four corners to generate tangential fireballs. There are four secondary air panels, five panels for mixing of primary air and coal powder, an overfire air panel, a bottom air panel, and a warmup oil panel in one windbox.

The boiler was generated into 3-D geometry using ICEM CFD. The furnace geometry used approximately 470,000 computational grid cells with 4 blocks, shown in Fig. 2. The properties of coal particle were set at: as-received HHV = 14.82 MJ/kg, volatile molecular weight = 30 kg/kmol, CO/CO_2 = 1 split in reaction products, high temperature volatile yield = 1.5, fraction of N in char = 0.7, and dry density = 800 kg/m^3. Coal particles are assumed to be spherical with mean diameter of 74 μm and temperature of 333 K. The particle properties were used in the discrete phase particle trajectory technique. The boundary conditions used for the CFD model were taken from the real operating condition in the power plant.

The standard k-ε model was used for the turbulent flow calculation [29]. The discrete ordinate (DO) radiation model was commonly used in coal combustion. Although the DO model demands on computational time, the model offers more detail and better accuracy [30]. The combustion model used is the eddy dissipation [22, 26]. The chemical equations for coal burned with oxygen, in a two-step reaction, are given below:

$$C+H+O+N+S+O_2 \Rightarrow CO+0.5H_2O+0.5N_2+SO_2 \quad (1)$$

$$2CO+O_2 \Rightarrow 2CO_2 \quad (2)$$

The inlet boundary condition was set to velocity inlet. The outlet boundary condition was set to outflow at the top of geometry. The wall boundary condition was divided into two parts; the bottom outlet was set to escape wall, all wall surface was set to no-slip condition, 4.57 mm thick with temperature = 673 K, internal emissivity = 0.8, and thermal conductivity of material = 1.5 W/m-K. The partial overall admittance factor is set as a constant value of 333 W/m^{2}K [22].

3 Results and Discussion

3.1 Slag Formation

Predicted mineral transformation, slag-liquid formation, and compositions of the sample coal are shown in Table 3. It was found that as the temperature increases to 950°C, slag-liquid starts to form. The main solids at 800°C are hematite, anhydrite, and high-albite. They decrease at higher temperatures. Unlike the main solid, the slag-liquid increase at higher temperatures. Fig. 3 presents total slag formation. The equilib model can be used to predict quantity and identify the details of slag-liquid formed and its composition at operating temperature, which can be applied to design operating temperature in the boiler furnace.

3.2 Ash Melting Temperature

The main compositions (SiO_2, Al_2O_3, CaO, and Fe_2O_3) of ash in the blended coal were chosen to plot against fusion temperature in ternery phase diagram. Fig. 4 presents the ash melting temperature predicted by the phase diagram. The lines show ash melting temperature for different compositions. The melting point of this coal is estimated to be 1440°C, which was in good agreement with measured AFT.

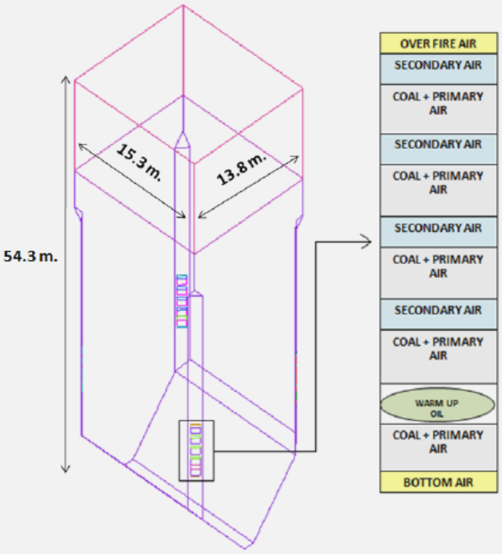

Fig. 1 Geometry of the Mae Moh boiler

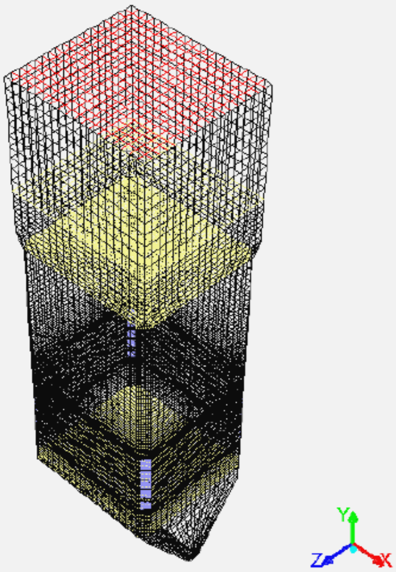

Fig. 2 Computational grid cells

The superimpose function in FactSage was used in the quaternery diagram. The possible reason for the behavior shown in Fig. 4 is that the combined effect of CaO, Fe_2O_3, SiO_2, and Al_2O_3 may be significant.

Table 3 Solid product from the FactSage Equilib model

Solid product (g/100 g of lignite)	Temperature (°C)								
	800	900	1000	1100	1200	1300	1400	1500	1600
Slag	0	0	0.7	5.4	8.7	10.6	14.2	14.4	14.3
composition									
Na_2O	0	0	0.4	0.6	0.4	0.3	0.2	0.3	0.4
K_2O	0	0	0.1	0.9	0.8	0.7	0.5	0.5	0.3
Al_2O_3	0	0	1.1	9.7	14.3	16.4	13.1	13.7	14.3
SiO_2	0	0	51.5	42.1	38.4	33.1	25.9	26.9	27.1
$NaAlO_2$	0	0	33.7	15.0	9.4	7.6	5.6	5.2	4.5
CaO	0	0	6.1	24.4	23.1	18.6	14.2	14.0	14.1
FeO	0	0	0.1	0.3	1.2	3.7	8.9	12.4	15.9
Fe_2O_3	0	0	0.2	1.6	5.2	12.4	26.0	21.6	18.0
MgO	0	0	5.2	4.6	6.5	6.8	5.1	5.1	5.1
MnO	0	0	1.1	0.1	0.1	0.1	0	0	0
TiO_2	0	0	0.3	0.7	0.5	0.4	0.3	0.3	0.3
Fe_2O_3 (Hematite)	5.1	5.1	5.1	5.0	4.5	3.1	0.0	0.0	0.0
$CaSO_4$ (Anhydrite)	4.9	4.9	2.5	0.0	0.0	0.0	0.0	0.0	0.0
$NaAlSi_3O_8$ (High-Albite)	2.9	2.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$Mg_2Al_4Si_5O_{18}$ (Cordierite)	1.8	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$Mg_4Al_{10}Si_2O_{23}$ (Sapphirine)	1.5	1.5	0.0	1.4	0.8	0.0	0.0	0.0	0.0
$KAlSi_2O_6$ (Leucite(RHF)-B)	1.1	1.1	1.1	0.8	0.8	0.6	0.4	0.0	0.0
Mg_2SiO_4 (Forsterite)	0.3	0.3	1.2	0.0	0.0	0.0	0.0	0.0	0.0
$CaAl_2Si_2O_8$ (Anorthite)	0.0	0.0	4.4	0.8	0.0	0.0	0.0	0.0	0.0
$NaAlSiO_4$ (Nepheline)	0.0	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0
$CaTiO_3$ (Perovskite-A)	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
$Ca_2MgSi_2O_7$ (Akermanite(melilite))	0.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0
$CaMg_2Al_{16}O_{27}$ (Solid)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

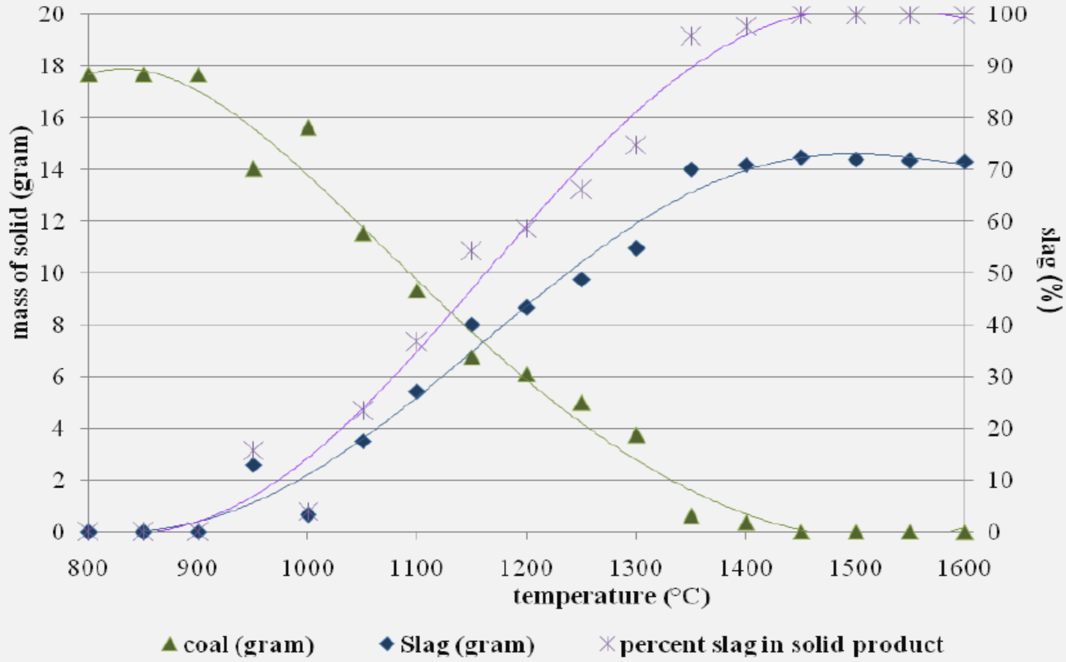

Fig. 3 Trend of slag formation

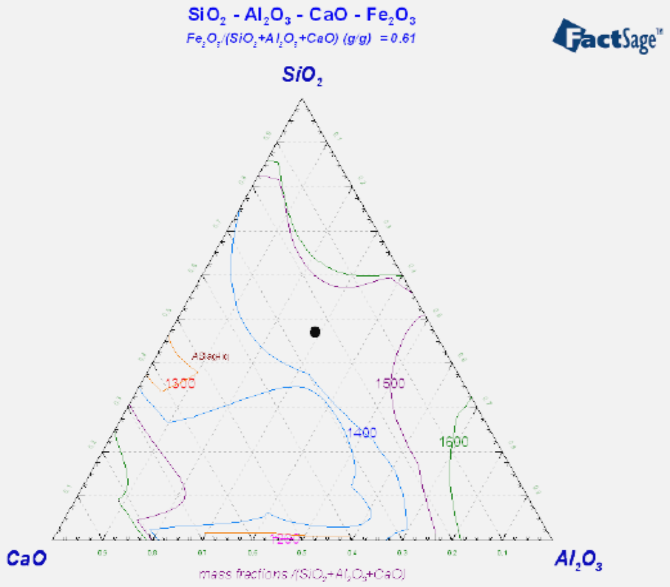

Fig. 4 Predicted ash melting point of the SiO_2-Al_2O_3- CaO,- Fe_2O_3 system

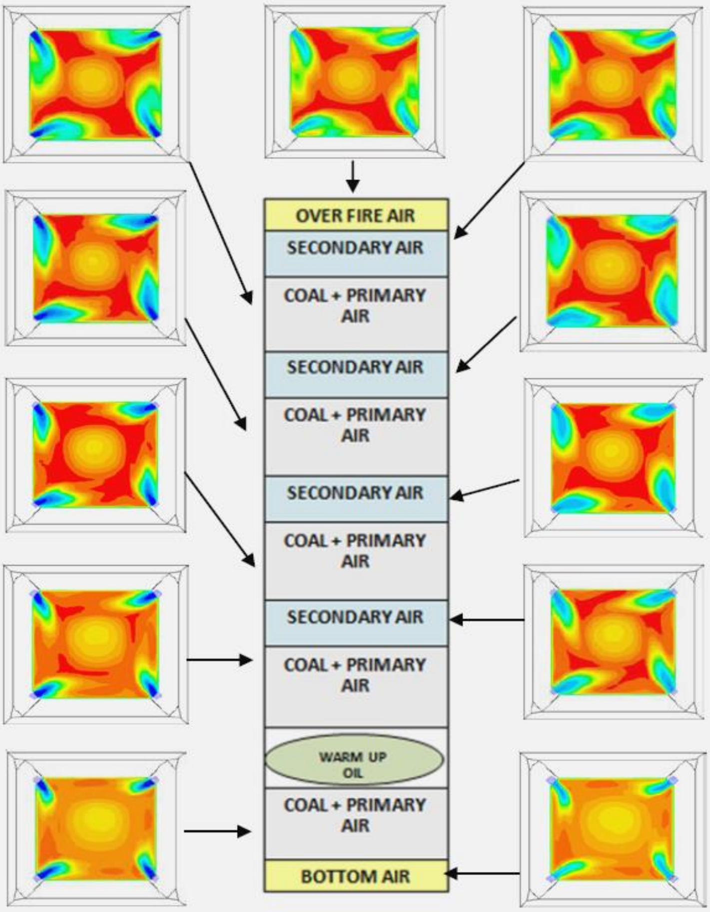

Fig. 5 Temperature distribution (in K) during coal combustion

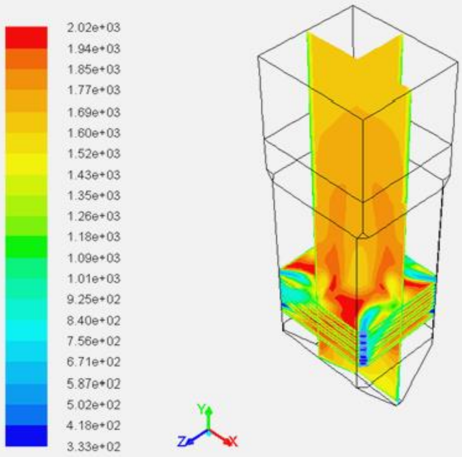

Fig. 6 Temperature distribution isosurface (K)

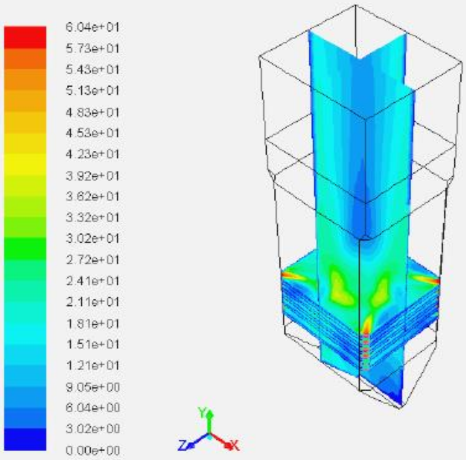

Fig. 7 Velocity distribution isosurface (m/s)

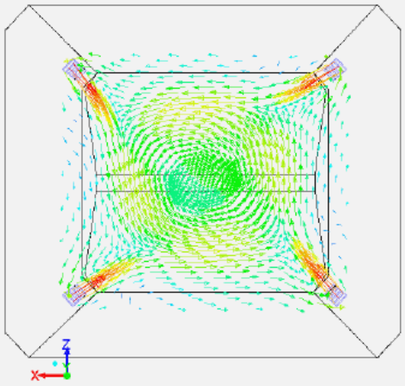

Fig. 8 Velocity vector in a cross section (m/s)

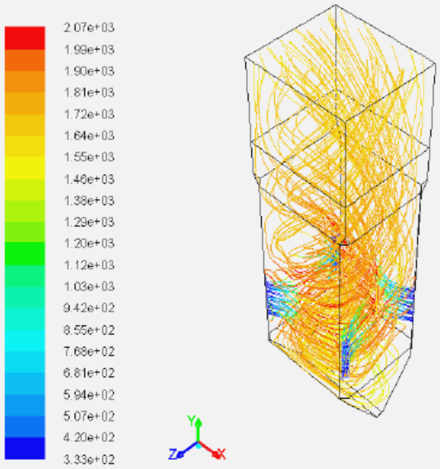

Fig. 9 Particle trajectory and temperature (K)

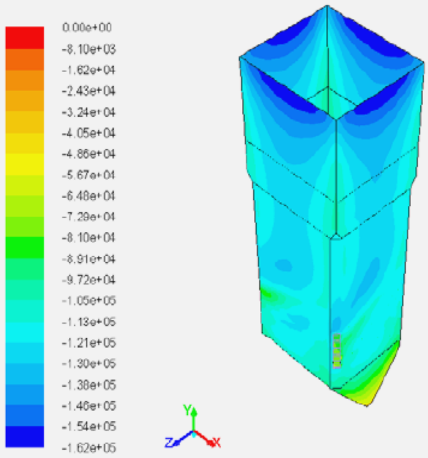

Fig. 10 Wall heat flux (W/m^2)

3.3 Potential Occurrence of Slag

The ANSYS CFD package has been used to calculate coal combustion in one of the Mae Moh boilers. Figs. 5 and 6 show the temperature distributions at different cross sections of the boiler furnace. Maximum temperature is located on the top of the windbox. The contour and direction of fireball velocity are shown in Figs. 7 and 8. Trajectory and tempeture of the coal particles are presented in Fig. 9. The distribution of wall heat flux is shown in Fig. 10. These results are used to predict deposition potential of slag inside the boiler furnace. The CFD simulation was conducted using the real operation information (coal properties and real operation) and it will be useful for comparison with the measured heat flux and flue gas outlet.

4 Conclusion

The equilibrium and phase diagram models were found to be useful in identifying composition of slag and predicting ash fusion temperature. The results from FactSage simulation can be used to compare with subsequent slag and ash fusion temperature experiments. The computational results of gas temperature distribution, flow fields, temperature and trajectory of particle, and surface heat flux appeared to show possibility of slagging deposition. The results of CFD simulation can be used to compare against wall heat flux and flue gas of EGAT measurements. This simulation is useful for predicting potential of slag in boiler and addressing future slag problem effectively.

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Characterization of slag from combustion of pulverized lignite with high calcium content in utility boiler

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Abstract

The Mae Moh mine in northern Thailand, with its abundant lignite, is the primary energy source for the Mae Moh power plant, which uses pulverized coal combustion in superheated boilers to generate electricity for domestic consumption. The lignite reserves remaining in the mine may contain up to 40% CaO. Given this high calcium content, more frequent and severe slagging problems are likely to occur. To better understand the potential slag problem, this research investigates the characteristics and properties of the slag by collecting and analyzing different samples of boiler slag from the Mae Moh power plant. Employing scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray fluorescence, and X-ray diffraction, the surface morphologies of the different slag samples were found to be similar. The majority of the crystal surfaces were agglomerates of particle-like clay and irregular granules stacked together. The most abundant elements in the slag were oxygen, aluminum, silica and calcium. The major chemical components included CaO, SiO_2, Al_2O_3, Fe_2O_3, and MgO. The minerals found in the slag were anorthite, gehlenite, akermanite, diopside, and esseneite. An increasing base-to-acid ratio reduced ash flow temperature. The Mae Moh lignite showed a medium to high slagging tendency. Increasing the slagging index led to a decrease in the ash fusibility temperature, due mainly to increasing amounts of Fe_2O_3 and CaO. From this study, the high CaO and Fe_2O_3 in the Mae Moh lignite clearly resulted in increased intensity of slag.

Keywords: Slag, Lignite, Ash deposit, Pulverized coal Combustion, Mae Moh

1. INTRODUCTION

Coal is a fossil-based fuel formed from organic sediments in ancient swamps. Subjected to heat and compression over considerable periods of time, this material was transformed into the various coal deposits that exist around the world (Graham *et al.*, 2011). A major fraction of current electricity consumption is provided by coal-fired power plants. At today's consumption rates, current coal reserves have been estimated to be about 200 years (Antonio and Eduardo, 2011). Thailand is the second largest coal producing country in Southeast Asia. Over 80% of Thailand's total annual lignite production comes from the Mae Moh surface mine in northern Thailand. All lignite mined at Mae Moh, about 15-17 million tons per year, supply feedstock to the Mae Moh power plant (Ewart, 2004). The Mae Moh power plant uses pulverized coal combustion (PCC) steam boilers with four 150 MW units and six 300 MW units, totaling 2,400 MW of capacity. The steam turbines are driven by superheated steam at temperatures and pressures of 530°C and 140 bars for the small units and slightly higher temperatures and pressures of 540°C and 161 bars for the larger units. The 10 units together can supply power of approximately 18,000 GWh per year, representing 28.3% of the total electricity production of the Electricity Generating Authority of Thailand (EGAT).

Each region of the mine produces lignite of slightly different characteristics. The typical chemical compositions of Mae Moh lignite are shown in Table 1. Blending management is required to meet the power plant's input fuel specifications. The mixed coal must have a sufficiently high heating value and meet sulfur content limitations. It was suggested by the original power plant manufacturer, and has been confirmed in subsequent studies by Pipatmanomai *et al*. (2009) and Luxsanayotin *et al*. (2010), that calcium oxide in the coal ash (CaO free SO_3) must not exceed 23% by weight. An assessment of the quality of the coal reserves at the mine revealed that the remaining lignite may contain up to 40% CaO. These high percentages may cause low temperature melting of ash. For PCC boilers, more frequent and severe slagging problems will create loss of capacity, loss of heat, boiler equipment damage, and additional maintenance costs in terms of both time and money.

Table 1. Properties of Mae Moh lignite with high calcium content.

Properties	Proximate analysis (%w/w as-received basis)				Heating value (%w/w dry basis)		Ultimate analysis (%w/w dry basis)				
	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	HHV (MJ/kg)	LHV (MJ/kg)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Sulfur (%)
Max.	34.38	41.86	16.63	28.53	18.30	17.61	48.94	3.08	1.81	12.90	4.11
Min.	30.71	37.65	13.84	22.19	15.68	15.00	45.29	2.54	1.59	11.95	3.60
Avg.	32.28	39.25	14.98	26.18	16.78	16.10	46.73	2.83	1.71	12.44	3.96

In a boiler chamber, the organic material in coal is combusted under high temperature and pressure; and the mineral matter transforms into ash, as shown in Figure 1. The ash particles adhere to the surface of the slag sinter layer, then melt into a liquid and finally transform to solid slag on furnace walls or other surfaces exposed predominately to radiant heat or excessively high gas temperatures (Singer, 1981; Seggiani, 1999; Song *et al*., 2009). An obvious impact of slag is reduced heat transfer. Slag is caused by many factors, such as the organic and/or mineral properties of the coal used, mineral transformation and decomposition, fluid dynamics, ash transport phenomena, vaporization and condensation of ash species, deposit chemistry-specie migration and reaction and heat transfer to and from the deposit (Borio and Levasseur, 1984). Although EGAT has made every effort to solve the problem, Mae Moh's coal is generally worse than others, and the issue is still not resolved. Pipatmanomai *et al.* (2009) studied the properties and composition of the lignite coal and ash that may affect the melting ash in the furnace of the PCC boilers. It was shown that the main components were Si, Al, Ca and Fe. Increasing CaO was believed to result in a lower melting temperature. The problem of the ash melting proportion of oxide is based on acids. Luxsanayotin *et al.* (2010) reported the composition of minerals in the Mae Moh lignite as a function of the melting temperature of the ash. X-ray analyses showed the presence of illite, pyrite and anhydrite in coal with 3.6% CaO. Anhydrite, known to lower the ash melting temperature, was found to be the most abundant mineral in coal with 40.4% CaO. However, properties related to slag formation have not been investigated. This study is an attempt to fill this gap. In this work, samples of boiler slag from the Mae Moh power plant were collected and analyzed. Slag characteristics and properties were investigated. The factors affecting the potential of slag occurrence were analyzed and discussed.

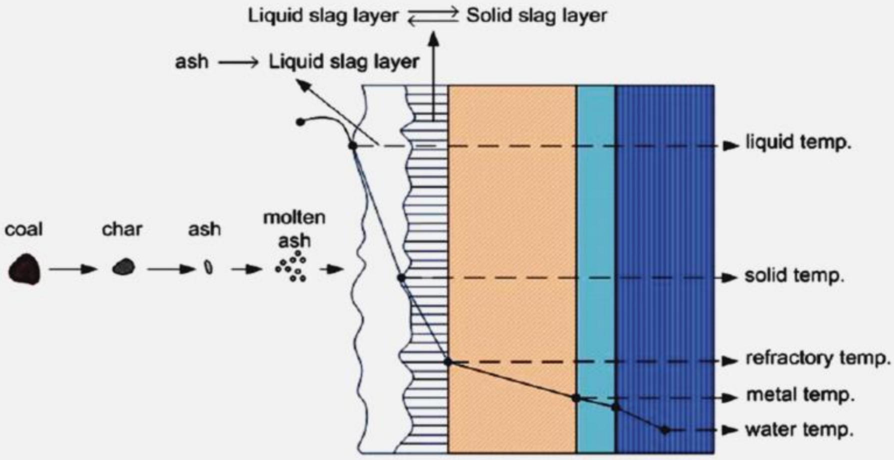

Figure 1. Mechanisms of slag deposit formation (Graham et al., 2011).

2. MATERIALS AND METHODS

2.1. Sampling and measurement

Samples of boiler slag with different appearances from a unit of the Mae Moh power plant were randomly collected and analyzed, qualitatively and quantitatively. For the high Ca content (>23% CaO free SO_3) test, the operational conditions were a combustion temperature of 950-1000°C and power generated at 87% of full load (about 260 MW). The properties of the ash produced were analyzed in order to assess the slag problem. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to describe the microstructural feature and chemical composition in slag deposition (Lopez *et al.*, 2003; Fernandez-Turiel *et al.*, 2004; Van Dyk, 2006; Van Dyk *et al.* 2009). The samples were prepared, dried and sized to no larger than 3 mm. Their top surfaces were coated with thin gold film to conduct electricity for analysis on a low vacuum SEM model JEOL JSM-5910LV at 15 kV and EDS. X-ray fluorescence (XRF) was used to analyze the chemical composition of ash and slag (Song *et al*. 2009). XRF measurements were conducted using a wavelength-dispersive sequential X-Ray spectrometer (Bruker AXS S4 EXPLORER) at 50 kV and 20 mA. X-ray diffraction (XRD) analyses will reveal the types of crystalline phases present in the slag. The identification of the crystalline phases provides an indication of the materials responsible for the slag problems and the temperatures to which the slag was exposed (Miller and Tillman, 2008). XRD is a very useful technique – and one of the most common and widely used methods (together with SEM) – for the identification and characterization of mineral matter and, to a lesser extent, inorganic amorphous matter and organic matter in fly ash (Stanislav and Christina, 2005). The samples were analysed by D8 X-ray Diffractometer Bruker AXS GmbH (40 kV, 40 mA, X-ray tube with Cu anode K-Alpha, step size of 0.04∞, step time of 1 s, scanning speed between 2q of 1-140∞ and temperature of 25°C).

2.2. Base-to-acid ratio analysis

The deposition behaviour was evaluated in terms of base-to-acid ratio (B/A) using Eq. (1) (Pipatmanomai *et al*., 2009; Song *et al*., 2009; Agraniotis *et al*., 2009). The B/A ratio is an indication of the fusion characteristics and slagging potential of coal ash and ash-containing metals to combine in the combustion process to produce low melting salts. The slagging potential of the B/A ratio defines the lower range of the slag at less than 0.2. Values between 0.2-1.0 indicate medium deposition tendency and values greater than 1.0 indicate high potential (Agraniotis *et al*., 2009). The main ash compositions, Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, CaO, TiO_2, Fe_2O_3 and MnO_2, were used to calculate B/A ratio.

$$\frac{B}{A}=\frac{Fe_2O+CaO+MgO+Na_2O+K_2O}{SiO_2+Al_2O_3+TiO_2} \qquad (1)$$

2.3. Slagging index analysis

The slagging index (R_s) of a coal has traditionally been taken as a measure of the slagging propensity of the ash (Russell *et al*., 2002). This value indicates the trend in slagging similar to B/A ratio, and was calculated from Eq. (2). It is normally combined with other indices, such as ash fusibility, to observe the slagging tendency more clearly. A high value results in an increased slagging potential. It was calculated from

$$R_s = B/A\,ratio \times Fe_2O_3 \qquad (2)$$

2.4. Ash flow temperature analysis

Ash flow temperatures (AFT) were analysed following the ash fusibility standard

(ASTM D1857-04). This property provides an indication of ash agglomeration and ash clinkering during combustion, in line with the tendency of ash to slag (Singer, 1981). AFT consists of four temperatures: initial deformation temperature (IT), softening temperature (ST), hemispherical temperature (HT) and fluid temperature (FT) (Song *et al*., 2009; Seggiani, 1999). The ash composition and B/A ratio were used as parameters for correlating ash fusibility with its composition.

2.5. Ash fusibility analysis

Ash fusibility provides an indication of ash agglomeration and ash clinkering during combustion (Singer, 1981). This parameter was calculated from Eq. (3). A calculated value in the range of 1052-1232°C indicates high slagging potential. If it is less than 1052°C, severe slagging potential is very likely to occur (McLennan *et al*., 2000; Dunnu *et al*., 2010).

$$Ash\ \ fusibility = \frac{4IT + HT}{5} \tag{3}$$

3. RESULTS AND DISCUSSION

3.1. Physical appearances

Representative boiler slag samples are shown in Figure 2. They appear as: (a) dark brown to black with a shiny surface, riddled with small and large holes (b) brown like cement, large but fragile (c) brown with small holes, hard but brittle (d) brown, like a fusion of lava, full of holes, crystals contain a large amount of sand-like substances.

Figure 2. Slag samples from the combustion of Mae Moh lignite with high Ca content.

3.2. Surface morphologies

SEM was used to examine the surface morphology of these slag samples. Elemental identification analyses of the samples were obtained by EDS. The results of the SEM images are presented in Figure 3. Although the macroscopic appearances of the collected slag were different, the characteristics of the surface of the SEM analysis with any random two samples indicated that they were not different. The majority of the crystal surfaces were agglomerates of particle-like clay and irregular granules stacked together.

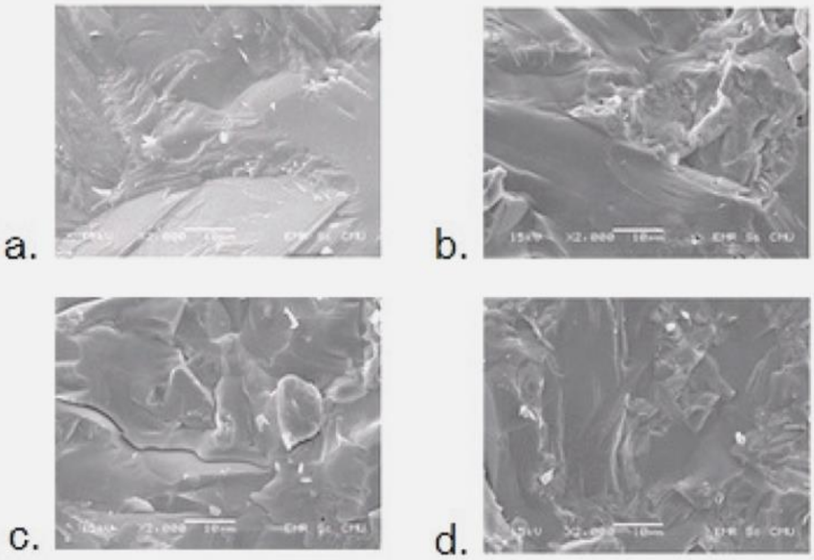

Figure 3. Surface morphologies of slag samples.

3.3. Elemental compositions

The data from SEM-EDS compared with X-ray fluorescence spectrometry (ASTM D4326) from the Mae Moh power plant are shown in Table 2. The main ash compositions were found to be Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, CaO, TiO_2, Fe_2O_3 and MnO_2. Results of slag elemental compositions are presented in Table 3. The slag was found to have an abundance of oxygen, aluminum, silica and calcium, which were probably quartz (SiO_2) (Luxsanayotin *et al*., 2010; Van Dyk *et al*., 2009; Van Dyk, 2006), anorthite ($CaAl_2Si_2O_8$) (Fernandez-Turiel *et al*., 2004; Li *et al*., 2011), mullite ($Al_6Si_2O_{13}$) (Li *et al*., 2011), gehlenite ($Ca_2Al_2SiO_7$) (Li *et al*., 2011), kaolinite ($Al_2Si_2O_7$) (Fernandez-Turiel *et al*., 2004; McLennan *et al*., 2000; Li *et al*., 2011) and calcium oxide (CaO) (Querol *et al*., 1995). Quartz and kaolinite are major mineral phases of coal during combustion in a large power station; and quartz, mullite and calcium oxide are major inorganic phases in slag (Querol *et al*., 1995). The chemical reaction during the combustion of mullite and calcium oxide produces anorthite at 950°C. The reaction between anorthite and calcium oxide is gehlenite, according to Eqs. (4) and (5) (Li *et al*., 2011). Iron, magnesium and potassium were also found. These are iron alumino-silicate ($FeO+SiO_2+Al_2O_3$) (McLennan *et al*., 2000; Li *et al*., 2011) and siderite ($FeCO_3$) (Van Dyk, 2006; McLennan *et al*., 2000; Agraniotis *et al*., 2009; Ram *et al*., 1995). Inorganic elements, Ca, and Mg – dissolved salts in the pore waters of coal, may have lower melting points (Li *et al*., 2011).

$$mullite\ (Al_6Si_2O_{13}) + calcium\ \ oxide\ (CaO) \overset{950°C}{\rightarrow} anorthite\ \left(CaAl_2Si_2O_8\right) \quad (4)$$

$$anorthite\ \left(CaAl_2Si_2O_8\right) + calcium\ \ oxide(CaO) \rightarrow gehlenite\ \left(Ca_2\,Al_2SiO_7\right) \quad (5)$$

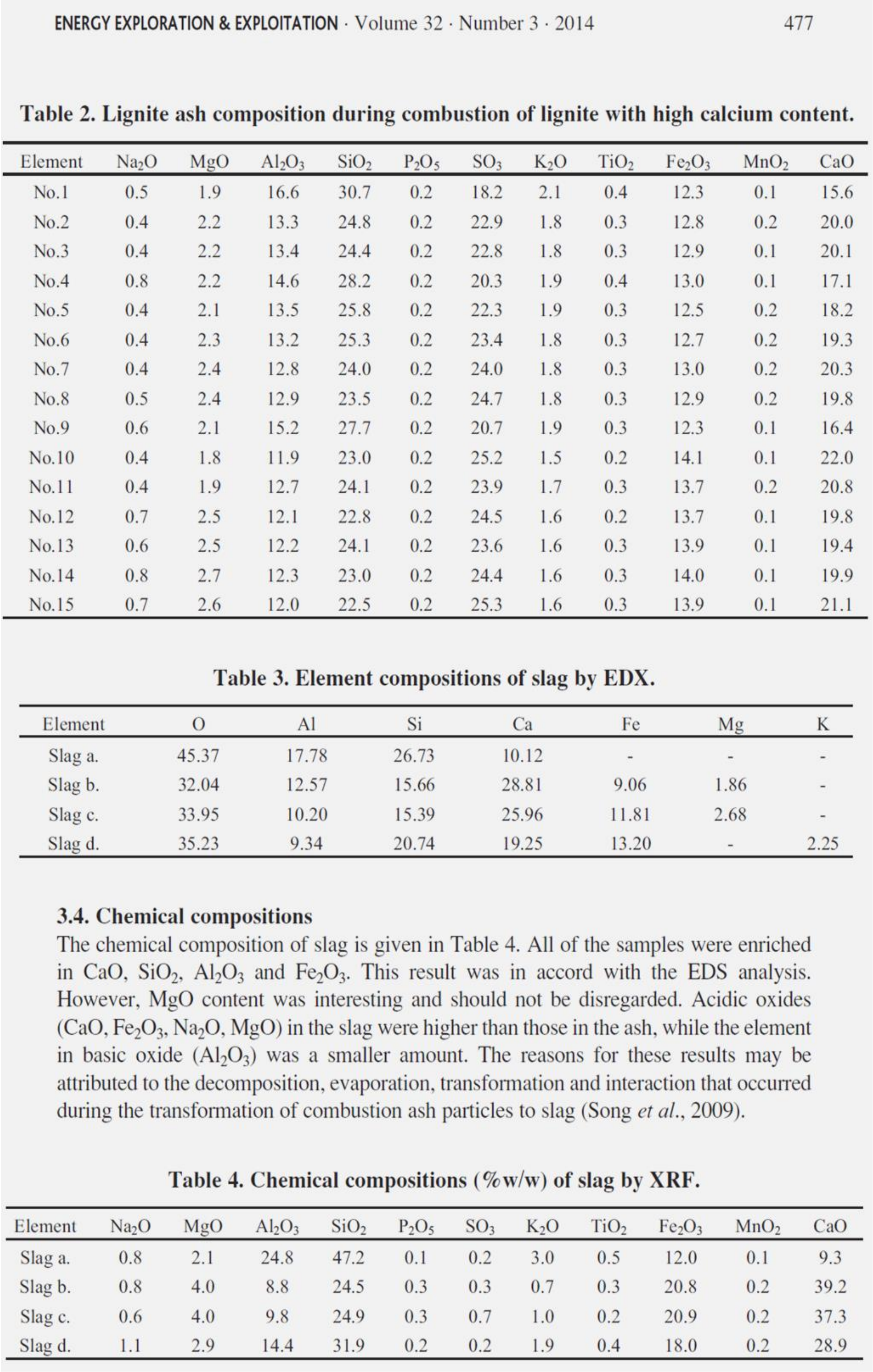

Table 2. Lignite ash composition during combustion of lignite with high calcium content.

Element	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	TiO_2	Fe_2O_3	MnO_2	CaO
No.1	0.5	1.9	16.6	30.7	0.2	18.2	2.1	0.4	12.3	0.1	15.6
No.2	0.4	2.2	13.3	24.8	0.2	22.9	1.8	0.3	12.8	0.2	20.0
No.3	0.4	2.2	13.4	24.4	0.2	22.8	1.8	0.3	12.9	0.1	20.1
No.4	0.8	2.2	14.6	28.2	0.2	20.3	1.9	0.4	13.0	0.1	17.1
No.5	0.4	2.1	13.5	25.8	0.2	22.3	1.9	0.3	12.5	0.2	18.2
No.6	0.4	2.3	13.2	25.3	0.2	23.4	1.8	0.3	12.7	0.2	19.3
No.7	0.4	2.4	12.8	24.0	0.2	24.0	1.8	0.3	13.0	0.2	20.3
No.8	0.5	2.4	12.9	23.5	0.2	24.7	1.8	0.3	12.9	0.2	19.8
No.9	0.6	2.1	15.2	27.7	0.2	20.7	1.9	0.3	12.3	0.1	16.4
No.10	0.4	1.8	11.9	23.0	0.2	25.2	1.5	0.2	14.1	0.1	22.0
No.11	0.4	1.9	12.7	24.1	0.2	23.9	1.7	0.3	13.7	0.2	20.8
No.12	0.7	2.5	12.1	22.8	0.2	24.5	1.6	0.2	13.7	0.1	19.8
No.13	0.6	2.5	12.2	24.1	0.2	23.6	1.6	0.3	13.9	0.1	19.4
No.14	0.8	2.7	12.3	23.0	0.2	24.4	1.6	0.3	14.0	0.1	19.9
No.15	0.7	2.6	12.0	22.5	0.2	25.3	1.6	0.3	13.9	0.1	21.1

Table 3. Element compositions of slag by EDX.

Element	O	Al	Si	Ca	Fe	Mg	K
Slag a.	45.37	17.78	26.73	10.12	-	-	-
Slag b.	32.04	12.57	15.66	28.81	9.06	1.86	-
Slag c.	33.95	10.20	15.39	25.96	11.81	2.68	-
Slag d.	35.23	9.34	20.74	19.25	13.20	-	2.25

3.4. Chemical compositions

The chemical composition of slag is given in Table 4. All of the samples were enriched in CaO, SiO_2, Al_2O_3 and Fe_2O_3. This result was in accord with the EDS analysis. However, MgO content was interesting and should not be disregarded. Acidic oxides (CaO, Fe_2O_3, Na_2O, MgO) in the slag were higher than those in the ash, while the element in basic oxide (Al_2O_3) was a smaller amount. The reasons for these results may be attributed to the decomposition, evaporation, transformation and interaction that occurred during the transformation of combustion ash particles to slag (Song *et al.*, 2009).

Table 4. Chemical compositions (%w/w) of slag by XRF.

Element	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	TiO_2	Fe_2O_3	MnO_2	CaO
Slag a.	0.8	2.1	24.8	47.2	0.1	0.2	3.0	0.5	12.0	0.1	9.3
Slag b.	0.8	4.0	8.8	24.5	0.3	0.3	0.7	0.3	20.8	0.2	39.2
Slag c.	0.6	4.0	9.8	24.9	0.3	0.7	1.0	0.2	20.9	0.2	37.3
Slag d.	1.1	2.9	14.4	31.9	0.2	0.2	1.9	0.4	18.0	0.2	28.9

3.5. Mineral components

The mineral components related to the chemical elements were similar to previous predictions and consistent with previous reports in the literature. Minerals found in the slag were anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), akermanite ($Ca_2MgSi_2O_7$), diopside ($CaMgSi_2O_6$), and esseneite ($CaFeAlSiO_6$). Anorthite was found in Slag a, the sample with the highest Si content. Gehlenite found in Slag b had the highest Ca content of the samples collected. Some of the elements found – akermanite, diopside, and esseneite – have never been reported before in the literature. Akermanite was found in Slag b and c. Slag b and c were fragile. Diopside found in slag c had high hardness, in a range of 5.5-6.5 (Anthony *et al*., 2001). Slag d was esseneite. Mg was not found in this slag. Its appearance, a fusion of lava and full of holes, differed from the others. It should be noted that XRD analysis was limited only to the crystal phases. This research was unable to determine the amorphous phases within the ash or deposits.

3.6. Relationship between ash chemistry and ash flow temperature

The X-ray fluorescence spectrometer showed that the major elements in the lignite ash were a combination of Al_2O_3, SiO_2, SO_3, Fe_2O_3 and CaO, together accounting for about 80%. This was consistent with the EDS results. Previous research indicated that CaO and Fe_2O_3 were very effective fluxes for aluminosilicates, giving rise to sticky ash particles and lowering the melting point of the ash (Singer, 1981). Increasing Al_2O_3 and SiO_2 were found to generally increase the IT. The calculated B/A ratios were plotted against AFT (Fig. 4). When the B/A ratios increased, AFT decreased. This was consistent with previous published results (Agraniotis *et al*., 2009), which showed that B/A ratios below 0.2 were likely to show low deposition. A value between 0.2-1.0 referred to medium deposition tendency, and values greater than 1.0 indicated a high deposition potential. For Mae Moh, values between 0.68-1.14 indicated a medium to high tendency. However, for B/A values greater than 1.00, the AFT pattern fluctuated slightly. This may be attributed to the fact that the amounts of tested ash on

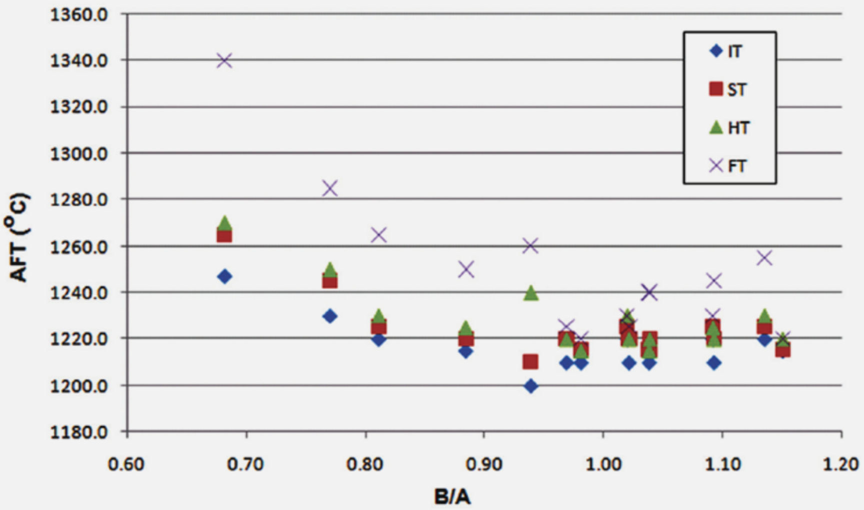

Figure 4. Ash fusion temperatures plotted against B/A ratio.

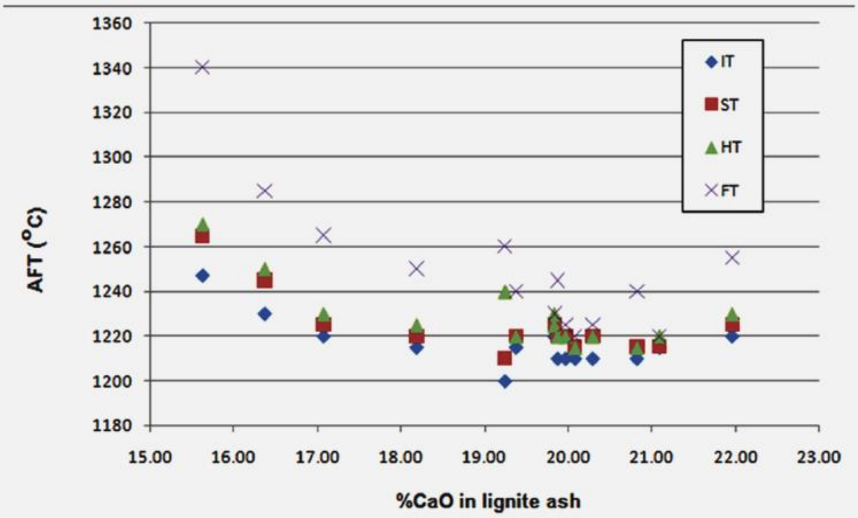

Figure 5. Ash fusion temperatures plotted against CaO in lignite ash.

the tip of the cone were very small, leading to slight variations in the composition as a result of incomplete mixing that, in turn, affected the AFT (Seggiani, 1999). In addition, when the effects of the B/A ratio and CaO content in the ash were compared, they showed similar patterns with respect to the AFT (Fig. 5). Other elements of the ash from this test did not have a significant effect on the AFT, except that Al_2O_3 and SiO_2 content raised the AFT.

The calculated R_s value and ash fusibility were used to create the relationship shown in Figure 6, revealing that when R_s increased, the ash fusibility temperature generally decreased. Within the ranges considered, the lowest R_s value appeared to have the highest fusibility temperature. This was consistent with the lowest amount of CaO and Fe_2O_3 contained in the sample. On the other hand, samples with the highest

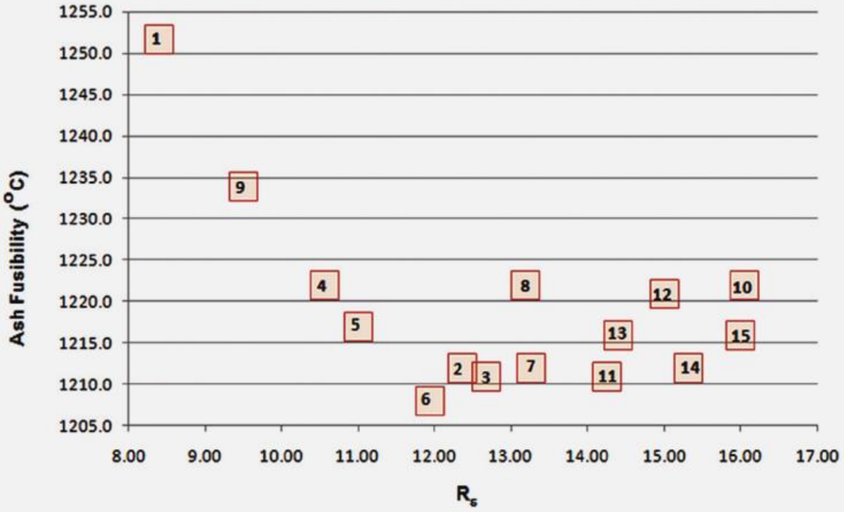

Figure 6. Relationship between ash fusibility with Rs values.

R_s did not have the lowest fusibility temperature. The ash fusibility distribution was similar to those R_s in the range of 10 to 17. These samples had slightly more Fe_2O_3 and CaO, when compared with sample no. 1. This finding was consistent with Russell *et al.* (2002), in which the synergistic effects were reported to show higher slagging potential, by a combination of Fe_2O_3 and CaO. Low values of R_s resulted in a small degree of ash accumulation. With high R_s, accumulation of ash was more severe.

4. CONCLUSIONS

In the present study, slag samples from a lignite-fired, utility boiler were collected. Slag from combustion of coal with high Ca content in the Mae Moh PCC boiler was characterized. Although macroscopic appearances of the samples differed visually. SEM analysis showed clearly that their microscopic surface morphologies were similar. A majority of the crystal surfaces were agglomerates of particle-like clay and irregular granules stacked together. The elements of oxygen, aluminum, silica and calcium were found in abundance in the slag. The major chemical constituents of the slag were CaO, SiO_2, Al_2O_3, Fe_2O_3, and MgO. The minerals found in the slag were anorthite ($CaAl_2Si_2O_8$), gehlenite ($Ca_2Al_2SiO_7$), akermanite ($Ca_2MgSi_2O_7$), diopside ($CaMgSi_2O_6$) and esseneite ($CaFeAlSiO_6$). For the interaction effect, increasing the B/A ratio reduced the AFT. For Mae Moh, the B/A ratio values were between 0.68-1.14, indicating a medium to high tendency for slagging. The relationship between ash fusibility and R_s values indicated that when the R_s increased, the ash fusibility temperature generally decreased. CaO and Fe_2O_3 in lignite ash were found to affect slagging significantly.

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Research Article

Nonisothermal Thermogravimetric Analysis of Thai Lignite with High CaO Content

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Thermal behaviors and combustion kinetics of Thai lignite with different SO_3-free CaO contents were investigated. Nonisothermal thermogravimetric method was carried out under oxygen environment at heating rates of 10, 30, and 50°C min^{-1} from ambient up to 1300°C. Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were adopted to estimate the apparent activation energy (E) for the thermal decomposition of these coals. Different thermal degradation behaviors were observed in lignites with low (14%) and high (42%) CaO content. Activation energy of the lignite combustion was found to vary with the conversion fraction. In comparison with the KAS method, higher E values were obtained by the FWO method for all conversions considered. High CaO lignite was observed to have higher activation energy than the low CaO coal.

1. Introduction

A significant proportion of the electricity generated in the world comes from pulverized coal-fired utility boilers. Thailand is the second largest coal-producing country in Southeast Asia. Over 80% of Thailand's total annual production comes from the Mae Moh surface mine in northern Thailand. Mae Moh coal is low grade lignite, containing relatively high percentages of ash and sulfur. The Mae Moh mine produces around 16 million tons of lignite per year to meet the 2400 MW capacity of Mae Moh's mine-mouth thermal power plant [1]. According to the Thailand power development plan for the period 2012–2030, electricity supply from coal remains a significant contributor to the future energy mix [2]. Considerable reserves of poor quality coal will have to be utilized efficiently with minimum impact to humans and the environment.

Characteristics of the lignite in the different regions of the Mae Moh mine vary greatly from the design coal. Blending of the coals is normally adopted to increase fuel flexibility, improve the performance of coals, and extend the range of usable coals [3]. The low grade coals can be mixed with the better grade ones to meet the power plant input fuel requirement, thus avoiding deterioration in the thermal performance of the power plant. For the current practice at the power plant, the mixed coal must have sufficiently high heating value under limitation of sulfur content, and CaO in ash on a SO_3-free basis must not exceed 23% w/w to prevent possible slagging problems [4, 5]. A recent survey of the lignite available in the remaining reserve suggests that coal blending may face mounting challenges because a major fraction of the coal mined will represent lignite with more than 40% CaO. Plant operations with lignite that contains increasingly higher CaO may be inevitable in the future.

A better understanding of the thermal decomposition and burning characteristics of this poor quality coal is crucial for safe and efficient operation of the boilers. Research on coal combustion may be performed using laboratory scale equipment. Thermogravimetric (TG) analysis is a simple and practical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The rate of mass loss as a function of temperature and time is measured, and the kinetic parameters in the thermal decomposition reaction are estimated [6, 7]. TGA has been used to study the combustion and kinetic behavior of various coal samples. It is commonly performed by an isothermal or nonisothermal procedure to understand the degradation behavior of coal and to estimate the kinetic parameters of char combustion or gasification [8]. A number of studies have been conducted on the kinetics of thermal decomposition of coals [9–13]. As for low rank coals, several recent reports have been published on the thermal decomposition kinetics [13–21].

There appears to be very few published reports on the combustion kinetics of poor quality coal [13]. Thai lignite is considered to be of poor quality because of its high sulfur (up to 5.5%) and ash content and because there is a large amount of SO_3-free CaO in its ash. So far, kinetic study on Thai lignite has been very rare [22, 23]. Furthermore, coals available currently and in future have different properties and compositions from those investigated in earlier reports. Nonisothermal isoconversional approach was not yet studied to any great extent. Therefore, in this paper, the burning characteristics of the lignite with different CaO contents were considered. Nonisothermal TG data at different heating rates was correlated with the kinetic parameters. Both Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were applied. The intrinsic kinetic from the TG analysis of the poor quality lignite will be useful for the design, modeling, planning, and understanding of the future operations of the power plant.

2. Material and Methods

2.1. Sample Preparation. The two different grades of lignite, based on the SO_3-free CaO content, were studied for thermal analysis. They were collected from different regions of the Mae Moh mine reserve and typically characterized as low and high CaO lignite samples. Prior to size reduction, they were dried in ambient. The samples were subsequently crushed in a hammer mill and sieved to the size of about 60 mesh. The ground lignite samples were dried and sent for analysis. The coal samples were analyzed in accordance with ASTM standards for proximate analysis (ASTM D 3176-07a, D 3173-03 (2008), D 3174-04, and D 3175-07), ultimate analysis (ASTM D 3176-89), sulfur in coal (ASTM D 5016-08), heating value (ASTM D 5865-10a), and ash composition (ASTM D 4326-04).

2.2. Thermal Measurements and Kinetics Modeling. Thermal analysis of lignite samples was carried out in a computer-controlled Perkin Elmer TGA 7 thermal analyzer. Prior to the experimental runs, the instrument was calibrated for precise temperature and weight readings. A quantity of 5.2 ± 0.1 mg of coal sample was used for each test. The digital microbalance is sensitive to 0.1 μg. Nonisothermal experimental runs were performed at three different heating rates of 10, 30, and 50°C min^{-1} under oxygen atmosphere. The flow rate of the carrier gas was maintained at 50 $\text{cm}^3\,\text{min}^{-1}$. The furnace temperature operated from ambient up to 1300°C. These dynamic runs were carried out on a platinum pan. The continuous records of weight loss and the weight loss rate with temperature were obtained. Thermal degradation behaviors were shown as TG and differential TG (DTG) profiles. They were also used as data for kinetics modeling.

For kinetics modeling, nonisothermal isoconversional approach was adopted in studying the kinetics of the Thai lignite. The approach has been shown to be able to estimate kinetic parameters without modeling assumptions [24, 25]. The kinetics of the thermal decomposition based on the rate equation for solid state decomposition processes [14] can be written as follows:

$$\frac{dx}{dt} = kf(x), \tag{1}$$

where x is the decomposed fraction of solid at time t, $f(x)$ is a function of x depending on the reaction mechanism, and k is the rate constant given by the Arrhenius equation for nonisothermal chemical reaction as

$$k = k_0 \exp\left(\frac{-E}{RT}\right), \tag{2}$$

where A is the preexponential factor, E is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. Replacing k with the Arrhenius equation gives

$$\frac{dx}{dt} = A \exp\left(\frac{-E}{RT}\right) f(x). \tag{3}$$

The decomposed fraction, x, found convenient to express a reaction by using a certain function $f(x)$, is defined in terms of the normalized change in mass of the sample as

$$x = \frac{w_0 - w_t}{w_0 - w_f}, \tag{4}$$

where w_0 is the initial weight, w_f is the final weight, and w_t is the weight at time t of the sample analyzed by the nonisothermal TG analysis.

The FWO method is [26]

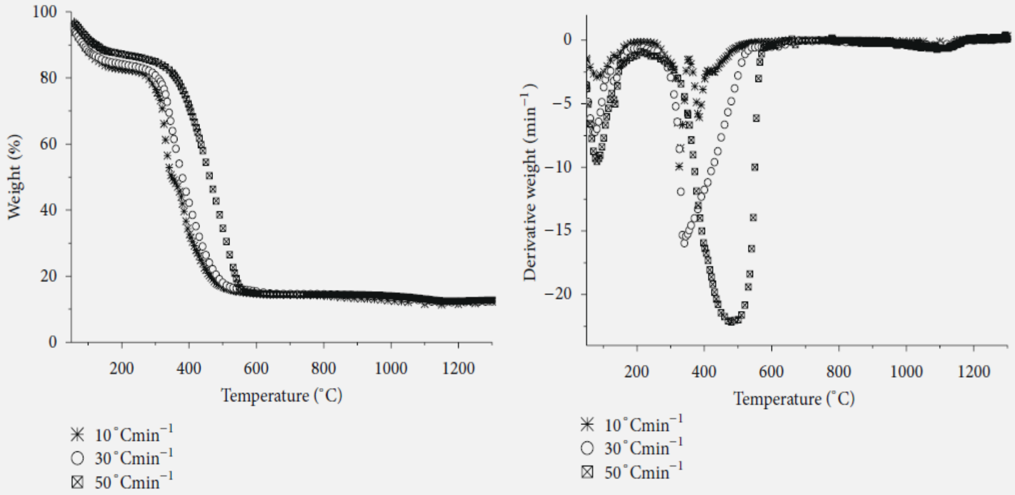
$$\ln\beta = \ln\left[\frac{AE_x}{Rg(x)}\right] - 5.331 - \frac{E_x}{RT_x}, \tag{5}$$

where β is the heating rate and $g(x)$ is the integral form of the $f(x)$. At a constant conversion, the plot of $\ln\beta$ versus $1/T$ obtained at several heating rates is approximated to be a straight line whose slope allows evaluation of the activation energy. The intercept can be obtained from the straight line and assumed to be first order of reaction from $f(x) = (1-x)$, and $g(x) = -\ln(1-x)$, and second order of reaction from $f(x) = (1-x)^2$ and $g(x) = (1-x)^{-1} - 1$, and third order of reaction from $f(x) = (1-x)^3$ and $g(x) = 0.5[(1-x)^{-2} - 1]$ [27–29].

The KAS method is as follows [26]:

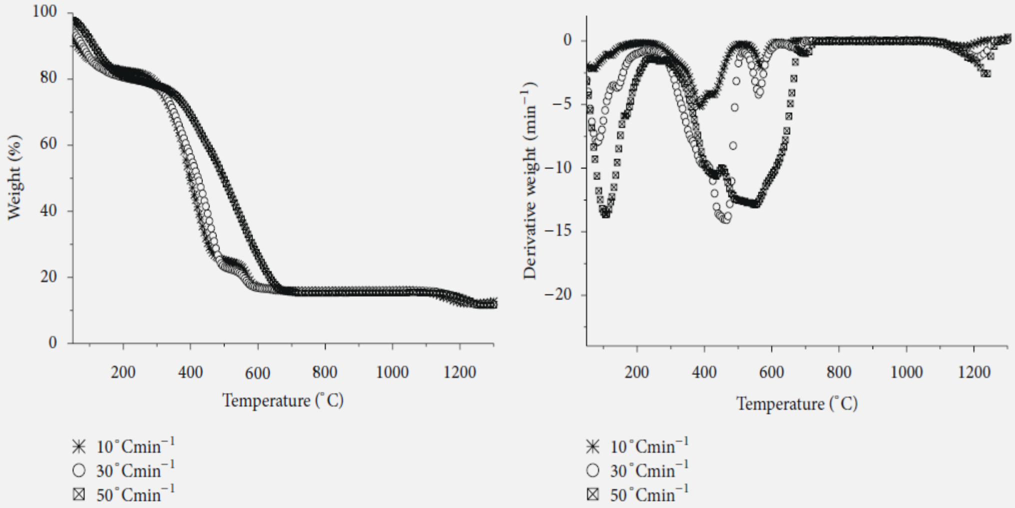
$$\ln\left(\frac{\beta}{T_x^2}\right) = \ln\left[\frac{AR}{E_x g(x)}\right] - \frac{E_x}{RT_x}. \tag{6}$$

The activation energy can be calculated from plotting $\ln(\beta/T_x^2)$ against $1/T$ and from the preexponential factor from the intercept of the resulting straight line.



(a) TG, low CaO lignite

(b) DTG, low CaO lignite



(c) TG, high CaO lignite

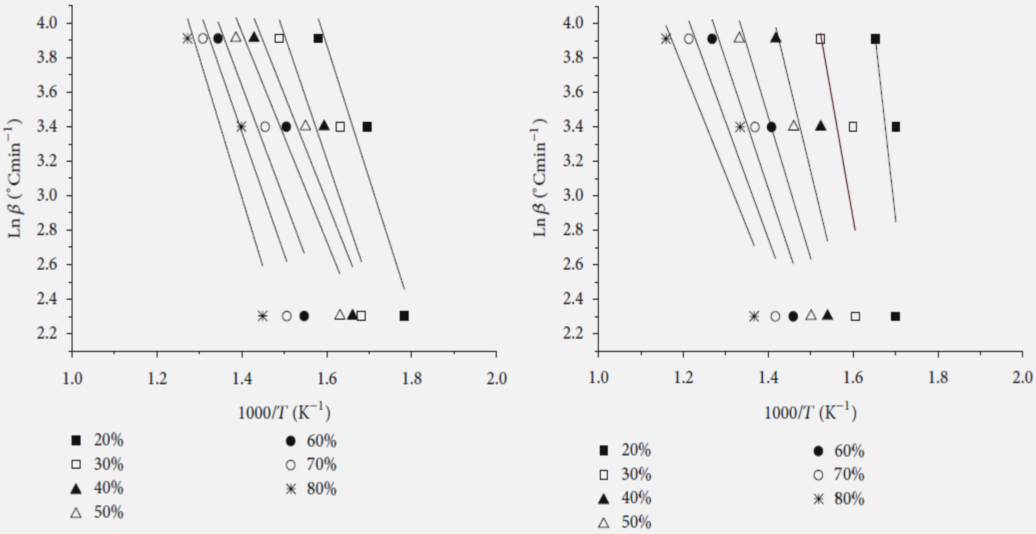
(d) DTG, high CaO lignite

FIGURE 1: Thermal degradation profiles of low and high CaO samples at different heating rates.

3. Results and Discussion

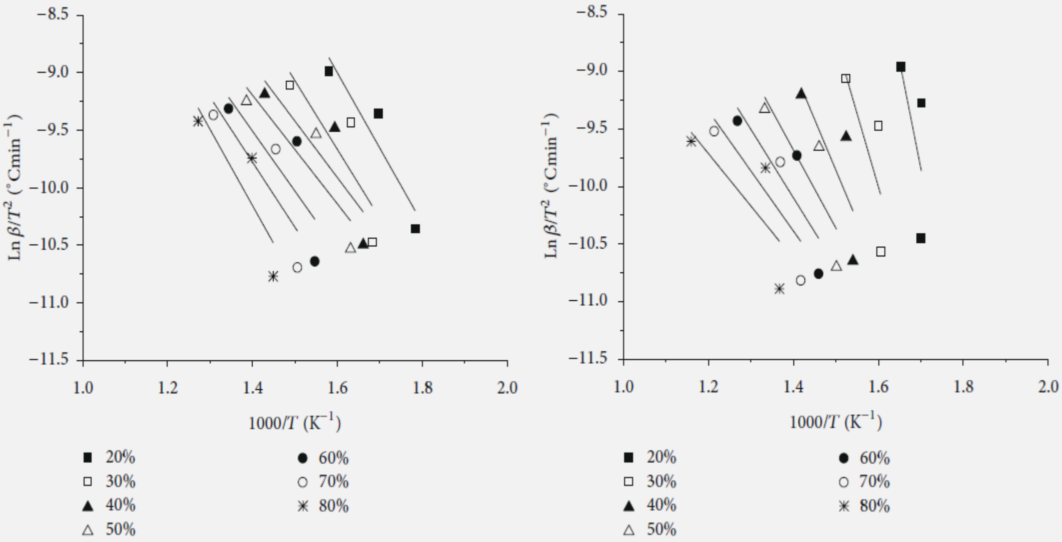
3.1. Coal Characteristics. A comparison of the results from the proximate and ultimate analyses and the calorific values of the two lignite samples, as well as their ash composition are shown in Table 1. It can be clearly seen that Mae Moh low rank coal is of poor quality, with extremely high moisture content (35–40% on as-received basis) and high S content (3.3–5.5% on dry basis). Their ash content is in the range of 17–20% on dry basis. While both low and high CaO lignite samples show similar calorific values, volatility, and CHO contents, their S contents differ markedly. As far as the amount of SO_3-free CaO in ash is concerned, the high CaO lignite has about three times more than the low CaO sample. The base-to-acid ratio of the former is about twice that of the latter, indicating higher slagging tendency.

3.2. Thermal Behaviors. The thermal characteristics of the coals were shown as change in weight with temperature (TG) and rate of weight loss (DTG) profiles. Figure 1 shows these degradation profiles of low and high CaO lignite samples at different heating rates. Continuous weight loss was evident. Both the lignite samples show similar TG patterns, suggesting that the same kinds of reactions occurred for all the heating rates considered, but the temperature ranges were different such that the TG curves shifted to higher temperatures as the heating rate increased. Three major weight loss stages can be characterized from the TG curves, corresponding to (i) the release of moisture in the sample, (ii) the release of volatile matter and combustion of char, and (iii) the decomposition of the mineral matter in the sample [16–18, 30]. For a given heating rate, the low CaO samples appeared to exhibit sharper



(a) (b)

FIGURE 2: Isoconversional determination of the kinetic parameters based on the FWO method for (a) low CaO and (b) high CaO lignite samples.



(a) (b)

FIGURE 3: Isoconversional determination of the kinetic parameters based on the KAS method for (a) low CaO and (b) high CaO lignite samples.

changes in the TG slope than the high CaO coal, consistent with the higher negative peaks of the DTG profiles. These observations were true for the first two stages. Higher heating rate was found to show wider temperature range for mass loss. The first stage of the low CaO lignite was from 50 to about 200°C, while the first stage of the high CaO lignite covered from 50 to about 250°C. The main release of organic components and the char combustion stage for the low and high CaO lignite samples were from 200 to 575°C and 300 to 700°C, respectively. The onset of the devolatilization was delayed for the higher CaO content lignite. Thermal degradation at this second stage of mass loss showed the peak rate for the low CaO lignite sample to be higher than that for the high CaO coal. From a comparison of the thermal degradation patterns, the reactions were found to take place at higher temperatures as the CaO content in the lignite increased.

TABLE 1: Analysis results of Thai lignite samples.

Characterization	Low CaO lignite	High CaO lignite
Proximate analysis (% w/w, as-received basis)		
Moisture content	35.1	39.6
Volatile matter	28.2	27.6
Fixed carbon	25.8	20.9
Ash	10.9	11.8
Ultimate analysis (% w/w, dry basis)		
C	58.5	58.4
H	3.0	2.4
N	1.9	1.8
O	12.9	12.6
S	5.5	3.3
Heating value (MJ/kg, dry basis)		
HHV	23.7	22.6
LHV	23.1	22.0
Ash compositions		
Na_2O	1.9	0.7
MgO	4.2	3.4
Al_2O_3	13.4	1.4
SiO_2	21.1	16.6
P_2O_5	0.1	0.2
SO_3	17.4	33.4
K_2O	1.3	0.2
TiO_2	0.3	0.1
Fe_2O_3	28.9	15.9
MnO_2	0.1	0.1
CaO	11.4	28.2
CaO (SO_3-free basis)	13.8	42.3
Base-to-acid ratio	1.37	2.68

Since both the coal samples have similar amounts of volatile matter, they would be expected to exhibit similar thermal degradation at similar ranges of temperature [18]. It was not yet clear if the presence of the higher CaO content may have contributed to this slight difference. Nonetheless, it should also be noted that, at a given stage of weight loss, the high CaO coal showed lower mass loss rate than the low CaO coal. Hence, the former was less reactive than the latter, if we take into account the direct proportionality between the peak loss rate and the reactivity. The findings implied that higher CaO containing lignite may require higher temperatures to react, but at slower rates.

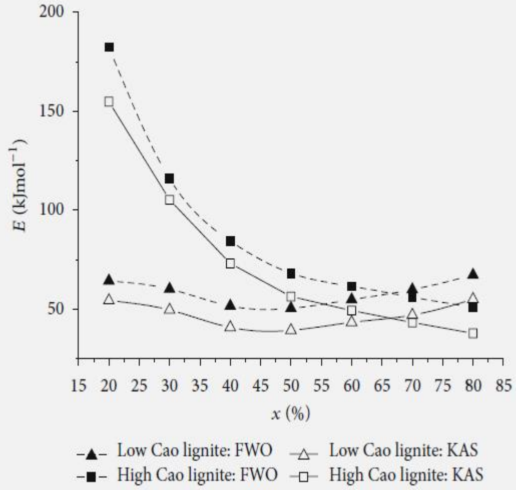


FIGURE 4: Dependency of apparent activation energy (E) on conversion (x), determined using the FWO and KAS methods for low and high CaO lignite samples.

3.3. Kinetic Analysis. The plot of $\ln \beta$ versus $1/T$ by the FWO method is shown in Figure 2. Three different heating rates were used, generating different Arrhenius plots at various conversions, from 20 to 80%. The apparent activation energy and preexponential factor were estimated from linear regression analysis for each conversion. Similarly, Figure 3 shows the relationships between $\ln(\beta/T_x^2)$ and $1/T$ by the KAS method at various conversions, from 20 to 80%. Straight lines were approximated and used to calculate relevant kinetic parameters. It should be noted that the quality of fittings was not very good. This may be caused by model and experimental system inadequacy and heat transfer limitations. Nonetheless, the variation of the activation energy with the extent of conversion is depicted in Figure 4. Similar relationships between the activation energy and conversion were observed between those obtained by the FWO and the KAS methods for the respective lignite sample. Within the conversion rates considered, the E values obtained from the FWO method appeared to be slightly higher than those from the KAS method. This was due to the distinctive linear approximation to the temperature integral. This observation was in agreement with those reported by Sis [18] and Xiao et al. [26]. Regarding the two lignite samples, the E values based on the FWO method for the high CaO coal were found to vary radically over the range of the conversion rate, decreasing from around 180 KJ mol^{-1} at $x = 0.2$ to 50 kJ mol^{-1} at $x = 0.8$, while those for the low CaO coal appeared to fluctuate slightly within the narrow band, about 65 ± 10 kJ mol^{-1}. Since the extent of conversion was directly related to temperature, the observed change in the E values should be attributed to the different reaction rates of dehydration, devolatilization, char combustion, and decomposition of mineral matter [16, 17]. Conversions in the 0–20% and 80–100% ranges occur in the lowest and highest ranges, hence they are associated mainly with the moisture release and mineral matter decomposition, respectively. In this work, the kinetic parameters were obtained in 0.2–0.8 conversion range; therefore, they were related mostly to the volatile release and char combustion. The average values of E and A assuming the first and second order of reaction are summarized in Table 2. The parameter A obtained were markedly different for the FWO and KAS

Table 2: Calculated combustion kinetic parameters.

Method	Material		n	Average	s.d.
FWO	Low CaO lignite	E (kJ/mol)		58.40	6.35
		A	1st	1.30×10^{-4}	1.04×10^{-4}
			2nd	2.13×10^{-4}	1.64×10^{-4}
			3rd	3.98×10^{-4}	3.08×10^{-4}
	High CaO lignite	E (kJ/mol)		88.55	46.87
		A	1st	1.58×10^{-5}	1.37×10^{-5}
			2nd	2.03×10^{-5}	1.72×10^{-5}
			3rd	4.72×10^{-5}	3.86×10^{-5}
KAS	Low CaO lignite	E (kJ/mol)		47.25	6.30
		A	1st	1.70×10^{-2}	1.03×10^{-2}
			2nd	2.84×10^{-2}	1.78×10^{-2}
			3rd	5.51×10^{-2}	4.18×10^{-2}
	High CaO lignite	E (kJ/mol)		74.35	42.21
		A	1st	1.88×10^{-2}	2.85×10^{-2}
			2nd	4.14×10^{-2}	7.04×10^{-2}
			3rd	1.10×10^{-1}	2.11×10^{-1}

methods, even for the 1st order reaction. However, the average activation energies obtained were in similar magnitude. The values of E by the FWO and KAS methods were calculated to be 58.4, 47.3 and 88.5, 74.4, for the low and high CaO lignite samples, respectively. The discrepancy between the two lignite samples may be attributed to the diversity in the composition nature and the structure of the samples. The implication from the findings was that the high CaO lignite sample may be less homogeneous than the low CaO coal.

4. Conclusion

In this study, the nonisothermal TG analysis of Thai lignite under highly oxidative environment was investigated at three different heating rates, up to 1300°C. The proximate and ultimate composition, sulfur in coal, calorific value, and ash composition of the low and high CaO lignite samples were analyzed. TG and differential TG curves were used to describe the different thermal degradation profiles for both the coal samples. Isoconversional kinetic analysis based on the FWO and KAS methods was found to be useful in evaluating the combustion kinetic parameters. It was observed that the apparent activation energy of coal combustion varied with the conversion fraction. The high CaO lignite was found to show higher activation energy than the low CaO coal.

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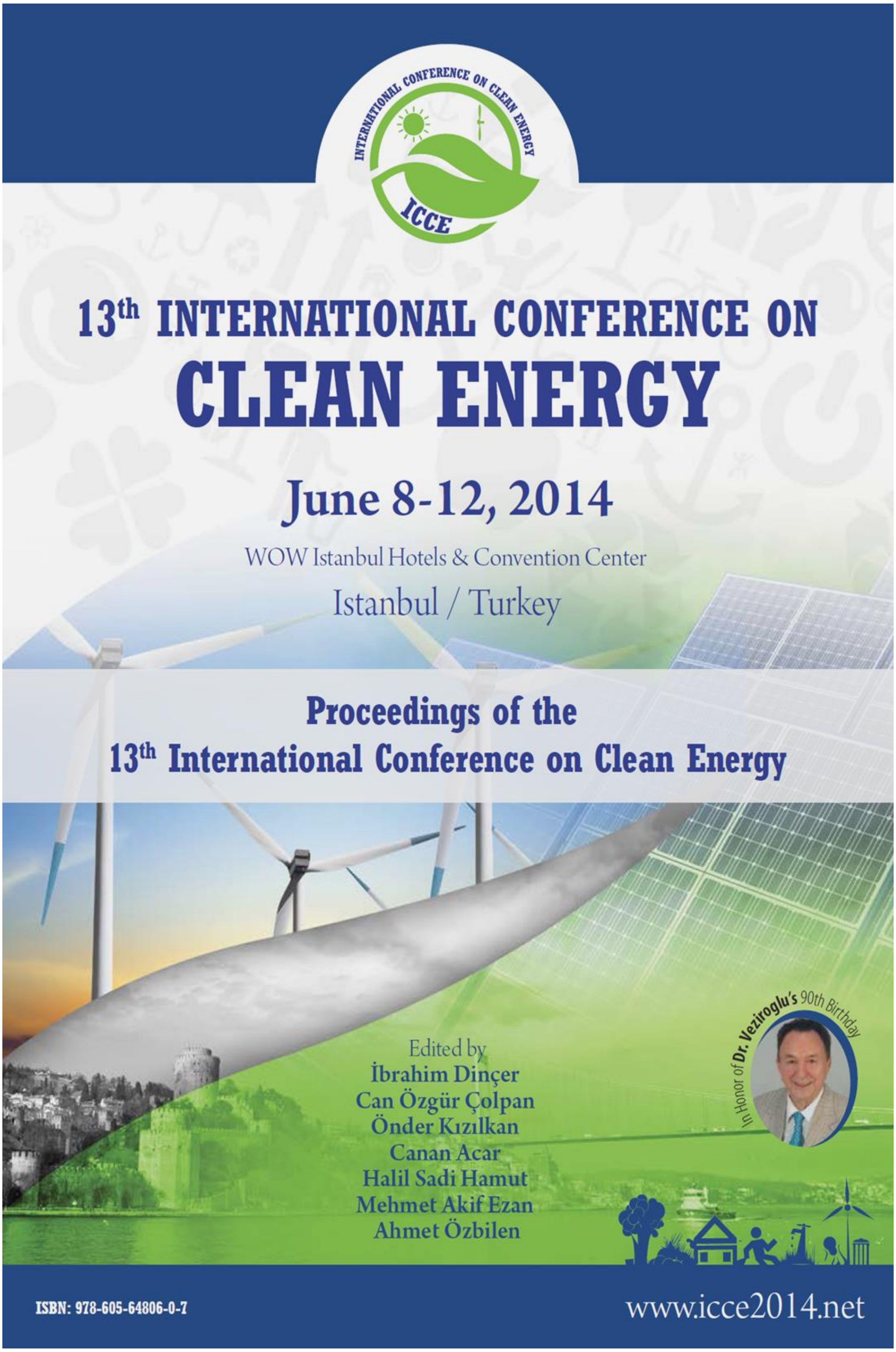

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ASSESSING POTENTIAL OCCURRENCE OF SLAG IN COMBUSTION OF THAI COAL BY EVALUATION OF THE ASH MELTING TEMPERATURE

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ABSTRACT

Slag from coal combustion for energy utilization causes many problems, such as loss of capacity, loss of heat, boiler equipment damage, loss of time and maintenance boiler costs. It is the low ash melting temperature that causes the severe slagging problem. In general, the ash fusibility temperature (AFT) analysis of coal is widely used to assess the ash fusibility and melting characteristics. In this study, two types of Thai lignite from the Mae Moh mine were collected and blended to produce seven fuels with different characteristics. The measured and predicted ash melting temperatures were derived from the AFT and FactSage^{TM} phase diagram module, respectively. The results obtained show that the measured AFT had a non-linear behavior with CaO content. The lowest ash melting point and initial deformation temperature – the fluid temperature gap were at 35.11% of CaO (free SO_3), 19.24% of SiO_2, 19.10% of Fe_2O_3, 3.38 of Al_2O_3, 3.24% of MgO, and 0.81% of Na_2O in coal ash. The main compositions in the coal ash (SiO_2, Al_2O_3, CaO, Fe_2O_3, Na_2O, and MgO) were used in the phase diagram module to predict the melting temperature. The simulated result from the SiO_2-Al_2O_3-CaO-Fe_2O_3 system was found to be similar in magnitude to the measured AFT. The SiO_2, Al_2O_3, CaO, and Fe_2O_3 in Thai coal ash appeared to significantly affect the slag behavior. It is clear from the findings that a good management of coal blending is necessary to reduce the future slagging problem.

1. INTRODUCTION

Combustion of pulverized coal is widely utilized throughout the World for power generation and it currently provides about 41% of the global electricity (Gubba et al., 2012). Thailand is the second largest coal producing country in Southeast Asia and over 80% of Thailand's total annual lignite production comes from Mae Moh surface mine in northern Thailand (Ewart, 2004). In 2012, the Electricity Generating Authority of Thailand (EGAT) was reported to have an installed generating capacity of 15,010 MW or over 46% of the country's gross energy generation. The lignite coal remains a major source of fuel in electricity generation which can generate the net energy of 32,500 GWh or about 19% nationally (EGAT, 2012).

Generally, lignite has a low calorific value. In addition, the Mae Moh lignite has a high ash, moisture and sulphur content. The available lignite is known to be of lower quality in the remaining mine areas (Juangjandee, 2010). Each region of the mine produces different characteristics of lignite and blending of coals from different regions is normally practiced at the power plant. The blended coal must have sufficiently high heating value, limit in sulphur content and CaO(freeSO_3) in ash. It was recommended that the CaO(freeSO_3) in ash of lignite for power plant must not exceed 23% w/w to prevent the slagging problems (Pipatmanomai et al., 2009; Luxanayotin et al., 2010; Pintana and Tippayawong, 2013). Occurrence of slag in a boiler furnace is schematically shown in Fig. 1. The radiation heat transfer to the water wall will decrease, leading to lower boiler efficiency. Further, soot blowers are unusually in high demand to remove the slag from the wall. Slagging problems can potentially result in loss of capacity, loss of heat, boiler equipment damage, loss of time, and money in maintenance of the boilers.

Slag consists of fused deposits or re-solidified molten material that forms primarily on the walls of the furnace or on other surfaces predominately exposed to the radiant heat or excessively high gas temperature (Singer, 1981). Slag is caused by many factors, such as the coal organic properties, coal mineral matter properties, mineral transformation and decomposition, temperature of the boiler furnace. For a better understanding of the potential of slag in boiler, the ash fusion temperature (AFT) is one of the crucial indicators widely used to indicate the potential of coal slagging (Song et al., 2009). A high ash melting point means low severity of slag. The FactSage^{TM} computer software and database can be successfully applied for the prediction of AFT, as well as for the development of blending strategies (Van Dyk and Keyser, 2012). The phase diagram module is used to visually the express liquidus temperature of slag. Good correlation between the coal AFT test and FactSage simulation results has been demonstrated (Song et al., 2010).

Although AFT has been routinely evaluated at the Mae Moh power plant, there appears to be only a few publications with regards to slagging of Thai lignites. So far the findings were not conclusive that the ash characteristics strongly affected low fusion temperature. Surprisingly, the correlation between measured and predicted AFT by FactSage phase diagram has not yet been explored in order to investigate potential of slag of Thai coal. So, the relation between AFT test and phase equilibrium diagrams is the main focus of this study.

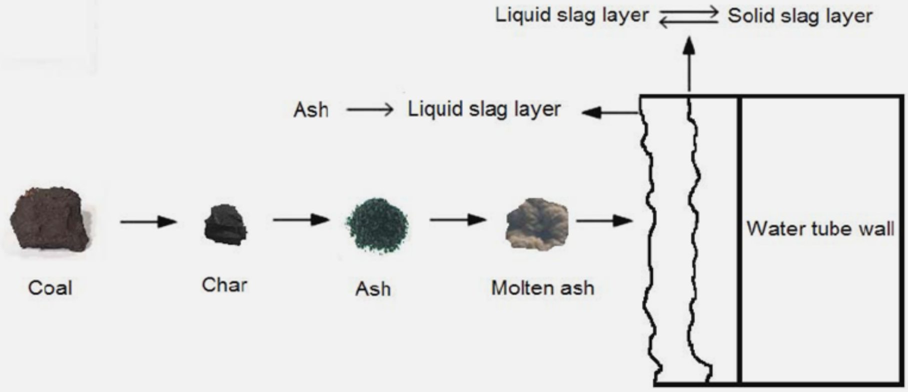

Fig. 1. Mechanism of slag formation in boiler furnace (adapted from Song et al., 2011).

Fig. 2. Critical temperature points as defined in ASTM Standard D 1857 (Singer, 1981).

2. METHODOLOGY

2.1. Sample Preparation

Lignites with high and low CaO (free SO_3) in ash were collected from the Mae Moh mine and blended to provide seven types of samples in this study. The blending of coal is required to vary the CaO (free SO_3) in the ash between 14 to 42%. Lignite A, B, C, D, E, F, and G were analyzed by a thermal gravimetric analyzer (ASTM D 3172-07a, D 3173-03, D 3174-04, and D 3175-07), Elemental analyzer (ASTM D 3176-09), and Bomb calorimeter (ASTM D 5865-07). X-ray fluorescence (ASTM D 4326) was used to analyze the chemical composition of the ash and slag. The CaO (free SO_3) content are calculated from

$$CaO_{freeSO_3} = CaO\,(100/(100 - SO_3)) \tag{1}$$

2.2. Determination of the ash fusion temperature

AFT was analyzed following the ASTM Standards D 1857 under an oxidizing environment. The oxidizing condition is significant in the formation of the deposits on the heating surface (Huggins et al., 1981). The test is based on the gradual thermal deformation of a pyramid-shaped ash sample, 19.05 mm in height and 6.35 mm in equilateral-triangular base width. Mounted on a refractory substrate, the sample is heated at a prescribed rate in a gas or electric furnace. During the heating process, changes in the shape of the pyramid are observed (Fig. 2). The following four characteristic deformation temperatures are reported (Song et al., 2009 a; 2009 b; Seggiani, 1999; Singer, 1981) :

1. Initial deformation temperature (IT): is the temperature at which the tip of the ash pyramid begins to show any evidence of deformation. Shinkage of the cone is ignored if the tip remains sharp.
2. Softening temperature (ST): is the temperature at which the ash sample has fused into a spherical shape in which the height is equal to the width at the base.
3. Hemispherical temperature (HT): is the temperature at which the ash sample has fused into a hemispherical shape where the height is equal to ½ the width at the base.

4. Fluid temperature (FT): is the temperature at which the ash sample has fused down into a nearly flat layer with a maximum height of 1.59 mm.

2.3. FactSage Modelling

The FactSage is the largest thermochemical package and database available for inorganic solids and slag. The FactSage package runs on a PC operating under Microsoft Windows and consists of a series of information, database, calculation, and manipulation modules (Bale et al., 2002; 2009; Van Dyk et al., 2006). FactSage modelling provides the ability to calculate and manipulate phase diagrams, established mainly in the field of complex chemical equilibrium and process simulations. It is used to supply insight into specific mineral interactions, slag formation and slag liquid temperatures of mineral compositions. The database can assist in the understanding, as well as predicting, what might happen with specific coal and mineral sources during the gasification or combustion processes. The phase diagram module is used to calculate, plot and edit phase diagram sections where the axes can be various combinations of temperature, pressure, chemical composition, etc. The input mole or mass fraction expressions can be reformulated (Bale et al., 2002; 2009; Eriksson and Konigsberger, 2008) and the phase equilibrium considered yields the lowest temperature of the ash when completely liquid (liquidus temperature) and the composition of solid and liquid phase at intermediate temperatures (Huggins et al., 1981).

In this study, mass fractions of ash composition of SiO_2, Al_2O_3, CaO, Fe_2O_3 (oxidizing conditions), Na_2O, and MgO and temperature were input into the FactSage software. The solution database used was FToxid-SLAGA for pure solids products with a pressure 1 atm. The superimpose function in the Figure module was used for the interface with the phase diagram. The composition point can be inserted to predict the ash fusion temperature. Initially, only the first three major components (SiO_2, Al_2O_3, and CaO) were considered for the ternary phase diagram. Subsequently, an additional component (chosen from Fe_2O_3, Na_2O, or MgO) was employed to simulate the quaternary phase diagram.

3. RESULTS AND DISCUSSION

The sample properties are shown in Table 1. Lignite A, (the raw coal with the lowest CaO(free SO_3) in ash) has the lowest moisture, but the highest volatile matter, fixed carbon and heating value, in contrast to Lignite G. Table 2 shows the ash composition of seven lignites, with varying CaO (free SO_3) in the ash in order of ascend. Table 3 shows results from the AFT tests in terms of average values and standard deviations. The scatter in the data was shown to be small, less than 7% of the corresponding average value. It should be noted that the ash at the tip of the cone in the AFT test can have slight variations from the overall composition, which may affect the measured AFT (Seggiani, 1999). The lignite E (35.11% of CaO (freeSO_3) in coal ash) was found to have the lowest ash melting point and IT-FT gap, thus indicating highest potential to a severe slagging problem.

Table 1. Mae Moh lignite properties.

	A	B	C	D	E	F	G
Proximate analysis (%w/w as-received basis)							
Moisture content	35.06	35.76	36.54	37.37	38.11	38.85	39.57
Volatile matter	28.17	28.21	28.23	28.05	27.86	27.79	27.58
Fixed carbon	25.86	25.00	23.83	22.72	22.05	21.36	20.93
Ash	10.91	11.03	11.40	11.86	11.98	12.00	11.92
Ultimate analysis (%w/w dry basis)							
Carbon (C)	58.54	58.49	58.49	58.43	58.41	58.39	58.35
Hydrogen (H)	3.00	2.95	2.95	2.72	2.63	2.55	2.44
Nitrogen (N)	1.89	1.86	1.86	1.86	1.86	1.84	1.81
Oxygen (O)	12.88	12.77	12.77	11.80	11.90	12.01	12.63
Sulphur (S)	5.49	5.35	5.35	4.76	4.29	3.94	3.33
Heating value (MJ/kg dry basis)							
HHV	22.80	22.76	22.58	22.44	22.38	22.27	22.08
LHV	22.15	22.12	21.97	21.86	21.81	21.73	21.55

Table 2. Mae Moh lignite ash composition.

	A	B	C	D	E	F	G
Composition (%mass)							
SiO_2	21.28	19.51	19.60	18.14	19.24	17.45	17.22
Al_2O_3	13.43	9.89	7.39	5.00	3.38	1.54	1.31
TiO_2	0.24	0.18	0.15	0.10	0.08	0.05	0.05
CaO	11.08	14.71	19.07	21.02	25.12	27.68	27.96
Fe_2O_3	28.03	24.83	22.93	20.03	19.10	16.19	15.98
Na_2O	1.87	1.47	1.30	1.04	0.81	0.67	0.74
MgO	4.02	3.57	3.45	3.22	3.24	3.24	3.46
K_2O	1.31	0.96	0.71	0.48	0.32	0.16	0.15
SO_3	18.64	24.73	25.22	30.71	28.47	32.73	32.86
P_2O_5	0.07	0.11	0.14	0.17	0.20	0.22	0.22
MnO_2	0.04	0.05	0.05	0.06	0.07	0.07	0.07
CaO(freeSO_3) (%mass)	13.62	19.54	25.50	30.34	35.12	41.15	41.64

Table 3. Mae Moh lignites ash deformation temperatures.

AFT (°C)	A		B		C		D		E		F		G	
	AVG	SD	AVG	SD	AVG	SD	AVG	SD	AVG	SD	AVG	SD	AVG	SD
IT	1235	69	1205	7	1205	18	1205	3	1205	6	1210	80	1235	31
ST	1305	10	1270	3	1230	13	1220	4	1215	2	1260	3	1260	14
HT	1340	14	1280	4	1235	15	1225	7	1220	3	1260	3	1265	18
FT	1480	5	1475	4	1250	20	1240	10	1225	3	1280	8	1300	21

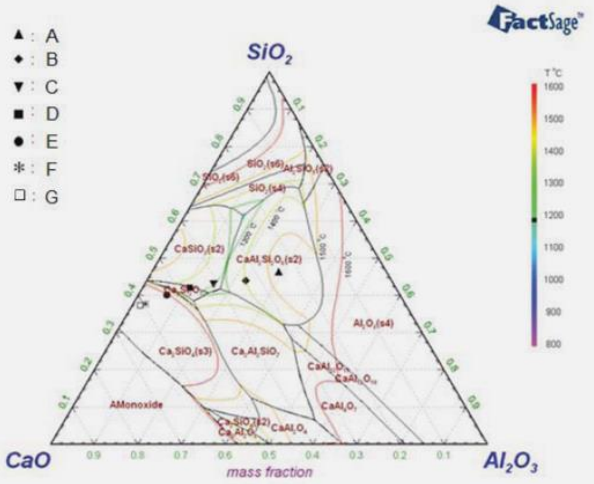

Fig. 3. Phase diagram for the SiO_2-Al_2O_3-CaO system.

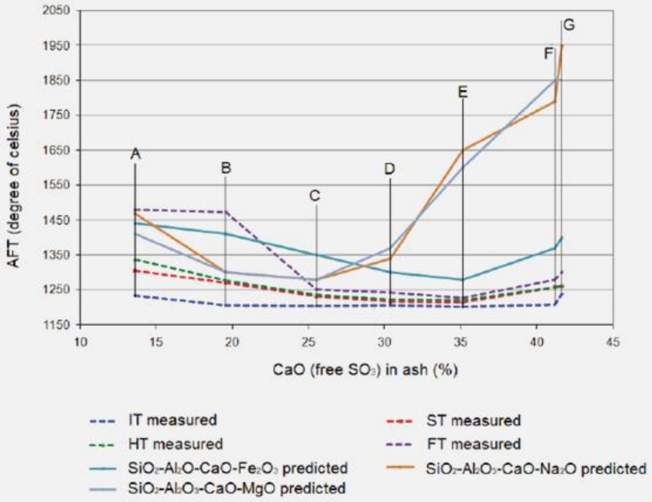

Fig. 4. Measured (dotted lines) and predicted (solid lines) ash fusion temperatures with different CaO(free SO_3) content in the ash.

In the simulation, the calculation can be extremely slow if all ash compositions are input into the module. Therefore only the main compositions (SiO_2, Al_2O_3, CaO, Fe_2O_3, Na_2O, and MgO) were used. The ternary phase diagram was calculated with the ash components on the control condition. Fig. 3 shows the change in the phase and the curves representing the liquidus temperatures from the SiO_2-Al_2O_3-CaO system. The mineral solid phases found in the results are $CaAl_2Si_2O_8$, $Ca_3Si_2O_7$, $CaSiO_3$, and Ca_2SiO_4. The AFT was found to decrease when the CaO content increased up to 25.50%, reaching the lowest value at 1300°C. However, it was predicted to increase at higher CaO contents. Similar patterns for the melting temperature were also observed with decreasing contents of acidic (SiO_2 and Al_2O_3) components. This predicted trend was similar to the measured AFT between 13.62-25.50 %CaO (free SO_3) content but a marked difference was observed between prediction and measurement for the %CaO (free SO_3) content from 30.34-41.64. This may be contributed to the fact that elements other than CaO may have strong influence on AFT.

It was therefore necessary to consider the phase diagram with four components. Three quaternary diagrams with varying temperature were used to predict the ash fusion temperature of SiO_2-Al_2O_3-CaO with Fe_2O_3, SiO_2-Al_2O_3-CaO with Na_2O, and SiO_2-Al_2O_3-CaO with MgO systems. The simulated results are shown in Fig. 4 along with the AFT from the measurement. They were found to exhibit a non-linear behavior with respect to the ash compositions. The effect of CaO in the ash on AFT was apparent. Unlike Na_2O and MgO, the quaternary system with additional Fe_2O_3 was found to be qualitatively and quantitatively similar to the measurement. The Fe_2O_3 appeared to be one of the major compositions affected by the ash fusion temperature. According to previous research on the SiO_2-Al_2O_3-CaO-Fe_2O_3 system, the lowest AFT was observed at 35% of the CaO content disregard of the SO_3 content (Song et al., 2010). The possible reason for this behaviour is that the SiO_2, Al_2O_3, CaO, and Fe_2O_3 may have an interaction effect that significantly influences the slagging potential.

From the findings, lignite E (35.12%CaO (freeSO_3), 19.24% SiO_2, 3.38% Al_2O_3, 25.12% CaO, and 19.10% Fe_2O_3) showed low fusion temperature, and may pose a severe slag problem when the boiler furnace temperature is above 1300°C. More details about the slag formation and slag liquid composition should be investigated using the FactSage Equilib module. Further, the predicted results can be compared with the SEM and XRD analysis results for a better understanding of boiler slag.

4. CONCLUSIONS

In this work, representative samples of blended Thai coal with different CaO (free SO_3) contents in ash were analysed for the AFT, and investigated for their slagging potential. Experimental measurements, as well as FactSage simulation of AFT were carried out. The results indicated that the lignite with 35% CaO (free SO_3) showed the lowest melting temperature in a range of 1300°C. This can pose a serious slagging problem when used. Also, it was shown that apart from SiO_2, Al_2O_3, and CaO, Fe_2O_3 was one of the main components influencing the slag formation. The predicted ash melting point from the SiO_2-Al_2O_3-CaO-Fe_2O_3

system of quaternary phase diagram has been shown to be in excellent agreement with for the measured AFT for Thai lignite. The SiO_2, Al_2O_3, CaO, and Fe_2O_3 system appeared to be capable of predicting the overall ash melting behaviour.

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NOMENCLATURE

AFT	ash fusibility temperature
Al_2O_3	aluminium trioxide
ASTM	American Society for Testing and Materials
AVG	average
C	carbon
$CaAl_2Si_2O_8$	anorthite
CaO	calcium oxide
$CaSiO_3$	wollastonite
Ca_2SiO_4	calcium silicate
$Ca_3Si_2O_7$,	rankinite
Fe_2O_3	furic oxide
FT	fluid temperature
H	hydrogen
HHV	high heating value, MJ/kg
HT	hemispherical temperature
IT	initial deformation temperature
K_2O	potassium oxide
LHV	low heating value, MJ/kg
MgO	magnesium oxide
mm.	millimeters
MnO_2	manganese dioxide
N	nitrogen
Na_2O	sodium oxide
O	oxygen
P_2O_5	phosphorus pentoxide
S	sulphur
SD	standard deviation
SEM	scanning electron microscopy
SiO_2	silica dioxide
SO_3	sulphur trioxide
ST	softening temperature
TiO_2	titanium dioxide
XRD	x-ray diffraction analyses

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Predicted formation and deposition of slag from lignite combustion on pulverized coal boilers

Pakamon Pintana, and Nakorn Tippayawong

Abstract**—**Lignite is the main source of energy used to generate electricity in Thailand. Slag in pulverized coal boilers is normally the main problem associated with combustion of this solid fuel. In this work, numerical simulation was applied to Mae Moh coal fired power plant. Prediction of ash melting points was used to identify possibility of slag formation. CFD simulation of the boilers' wall temperatures and coal particle trajectories were used to predict and assess deposition potential of slag inside the boiler. It was found to have great potential to quantitatively and qualitatively predict and identify formation and deposition of slag in the boilers.

Keywords**—**slag, pulverized coal combustion, ash deposition, CFD simulation

I. INTRODUCTION

LIGNITE coal is a major source of energy in the North of Thailand. But, it is usually of poor quality, with high moisture, sulfur, and ash contents. Under management of Electricity Generating Authority of Thailand (EGAT), Mae Moh power plant is a steam power plant that utilizes this lignite as fuel. Its pulverized coal boilers are generating electricity with the total capacity of 2,400 MW, accounting for about 12% of the national electricity consumption. The fuel consumption is about 15-17 million tons per year, obtaining from the Mae Moh mine.

A major operation challenge faces by EGAT engineers is management of ash. For a pulverized coal boiler, there is always slag in the furnace. Soot blowers normally operate to remove the slag from the wall. However, if slag in the boiler becomes excessive, the soot blowers may not be able to handle it, and radiation heat transfer decreases, leading to lower overall boiler efficiency. Subsequent problems associated with slag such as loss of capacity, loss of heat, boiler equipment damage, loss of time and money in maintenance boiler will occur.

Slag consists of fused deposits or a re-solidified molten material that forms primarily on the walls of the furnace or on other surfaces predominately exposed to the radiant heat or excessively high gas temperatures [1]. Slag is caused by many factors, such as the coal organic properties, coal mineral matter properties, mineral transformation and decomposition, temperature of the boiler furnace, the fluid dynamics, ash transport, vaporization and condensation of the ash species, deposit chemistry-specie migration and reaction etc. [2-3].

In this work, the slagging potential (combined effect of the slag liquid formation, ash flow distribution, and temperature profiles) in a pulverized coal fired boiler of EGAT Mae Moh power plant was investigated, using software programs.

II. METHODOLOGY

A. Lignite

The fuel properties of lignite coal were analyzed for proximate and ultimate composition, as well as its heating value. Additionally, its ash composition and ash fusibility temperatures were also analyzed [4-10]. Results are shown in Table 1.

B. Boiler Geometry

A furnace of 300 MWe Mae Moh tangentially fired boiler is shown in Fig. 1. The dimensions are 13.8 m in width and 15.3 m in breadth. The height from the lowest at hopper to the highest at the superheater and reheater is 54.3 m. On the walls, there are 4 windboxs for four corners to generate tangential fired balls. There are 4 secondary air panels, 5 panels for mixing of primary air and coal powder, an over fire air panel, a bottom air panel, and a warm up oil panel in 1 windbox.

C. FactSage Program

The FACTSAGE program has been developed as an efficient predictive tool for prediction of liquidus temperature, proportions of solids, mineral formation, and phase equilibria of ash samples [6-14]. FactSage is the fusion of two well-known software F*A*C*T/FACT-Win and ChemSage and it is the largest thermochemical package and database available for inorganic solid and slag in the field of computational thermochemistry. The package runs on a PC operating under Microsoft Windows [5].

The Equilib module (thermodynamic application calculations) and Phase Diagram module (phase diagram calculations) are used to incorporate the FactSage Gibbs energy minimizer [15]. It calculates the concentrations of chemical species when specific elements or compounds reacted or partially reacted, in order to reach a state of chemical equilibrium [16]. In this study, these modules were used to predict the ash behavior, the ash fusion temperature.

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Table 1 Coal and ash properties

Proximate analysis (% w/w, as-received basis)	
Moisture content	35.07
Volatile matter	28.17
Fixed carbon	25.86
Ash	10.91
Ultimate analysis (% w/w, dry basis)	
Carbon (C)	58.54
Hydrogen (H)	3.00
Nitrogen (N)	1.89
Oxygen (O)	12.88
Sulfur (S)	5.49
Heating value (MJ/kg dry basis)	
HHV	22.80
LHV	22.15
Ash composition (% w/w)	
SiO_2	21.28
Al_2O_3	13.43
TiO_2	0.24
CaO	11.08
Fe_2O_3	28.03
Na_2O	1.87
MgO	4.02
K_2O	1.31
SO_3	18.64
P_2O_5	0.07
MnO_2	0.04
Ash fusion temperature (°C)	
IT	1235
ST	1305
HT	1340
FT	1480

D. *CFD Simulation*

Computational fluid dynamics (CFD) has been used to simulate the firing of coal combustion under different operating conditions extensively [17-20]. In this work, a commercial CFD package, ANSYS Fluent, was used to predict gas flow, temperature distribution and particle trajectory that can adapt to predict slagging behavior [12, 21].

In generally, coal combustion in CFD models is used to solve for fluid flow, turbulence, particle trajectory, heat transfer, chemical reactions of the fuel, and the formation of pollutants [22]. In this study, FLUENT version 13.0 was used to predict the temperature and flow distribution inside a boiler. The wall heat flux was evaluated for comparison with real operating parameters. The information was combined with those from FactSage method to predict deposition of slag in the boiler furnace. All numerical simulation was performed at the University of Leeds.

A furnace was generated into 3-D geometry using ICEM CFD. The furnace geometry used approximately 470,000 computational grid cells with 4 blocks. The properties of coal particle was set at: as-received HHV = 14.82 MJ/kg, volatile molecular weight = 30 kg/kg mol, $CO/CO_2 = 1$ split in reaction products, high temperature volatile yield = 1.5, fraction of N in char = 0.7, and dry density = 800 kg/m^3. The boundary conditions used for the CFD model were taken from the real operating condition in Mae Moh power plant.

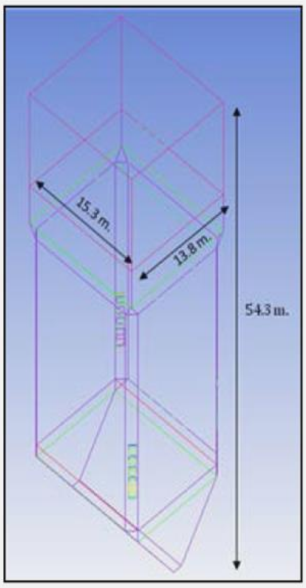

Fig. 1 The geometry of Mae Moh boiler

The inlet boundary condition was set to velocity inlet. The outlet boundary condition was set to outflow at the top of geometry. The wall boundary condition was divided into two parts; the bottom outlet was set to escape wall, all wall surface was set to no-slip condition, 4.572 mm thick with temperature = 673 K, internal emissivity = 0.8, and thermal conductivity of material = 1.5 W/m-K.

The RNG k-ε turbulence model was used. The Discrete Ordinate radiation model was commonly used in coal combustion. The combustion model used is the Eddy Dissipation with two step of chemical reaction.

III. RESULTS AND DISCUSSION

A. *Slag Formation*

Predicted mineral transformation and slag-liquid formation of the sample coal are shown in Table 2. It was found that as the temperature increases to 950°C, slag-liquid starts to form. The main solids at 800°C are hematite (Fe_2O_3), anhydrite ($CaSO_4$), and high-albite ($NaAlSi_3O_8$). They decreased at higher temperature. Unlike the main solid, the slag-liquid increased at higher temperature. Fig. 2 presents total slag formation. The equilib model can be used to predict quantity and identify the details of slag-liquid formed and composition at operating temperature, which can be applied to design temperature in the boiler furnace.

B. *Ash Melting Temperature*

The main compositions (SiO_2, Al_2O_3, CaO, and Fe_2O_3) in ash of blended coal were select to plot against with fusion temperature in ternery phase diagram. Fig. 3 presents the ash melting temperature predicted by phase diagram.

Table 2 The mineral matter output form Equilib model

Mineral composition (g/100g of lignite)	Temperature (°C)				
	800	1000	1200	1400	1600
Slag-liquid	0.0	0.7	8.7	14.2	14.3
Fe_2O_3	5.1	5.1	4.5	0.0	0.0
$CaSO_4$	4.9	2.5	0.0	0.0	0.0
$NaAlSi_3O_8$	2.9	0.0	0.0	0.0	0.0
$Mg_2Al_4Si_5O_{18}$	1.8	0.0	0.0	0.0	0.0
$Mg_4Al_{10}Si_2O_{23}$	1.5	0.0	0.8	0.0	0.0
$KAlSi_2O_6$	1.1	1.1	0.8	0.4	0.0
Mg_2SiO_4	0.3	1.2	0.0	0.0	0.0
$CaAl_2Si_2O_8$	0.0	4.4	0.0	0.0	0.0
$NaAlSiO_4$	0.0	1.2	0.0	0.0	0.0
$CaTiO_3$	0.0	0.1	0.0	0.0	0.0
$Ca_2MgSi_2O_7$	0.0	0.0	0.0	0.0	0.0
$CaMg_2Al_{16}O_{27}$	0.0	0.0	0.0	0.0	0.0

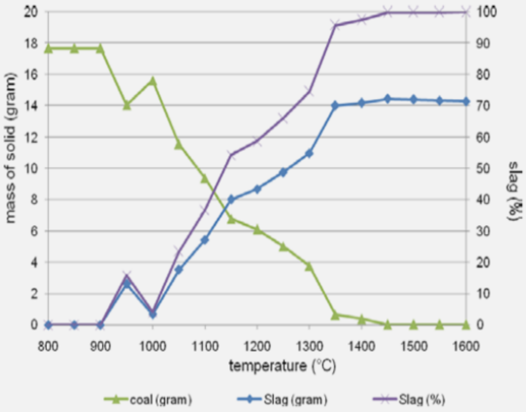

Fig. 2 Trend of slag formation

The superimpose function in FactSage was used in quaternery diagram. The possible reason for this behaviour is that the CaO, Fe_2O_3, SiO_2, and $Al_2O_3$are significantly.

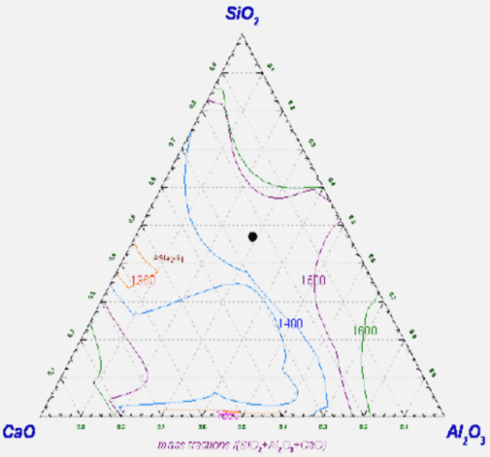

Fig. 3 Predicted ash melting point of SiO_2-Al_2O_3-CaO-Fe_2O_3 system

C. *Potential of Slag Deposition*

CFD simulation results are shown in Figs. 4-6. The wall temperature and the particle trajectory were applied with predited deposition potential of slag inside the boiler furnace. The CFD simulation was conducted using the real operation information (coal properties and real operation) and it will be useful for comparison with the measured heat flux and flue gas outlet.

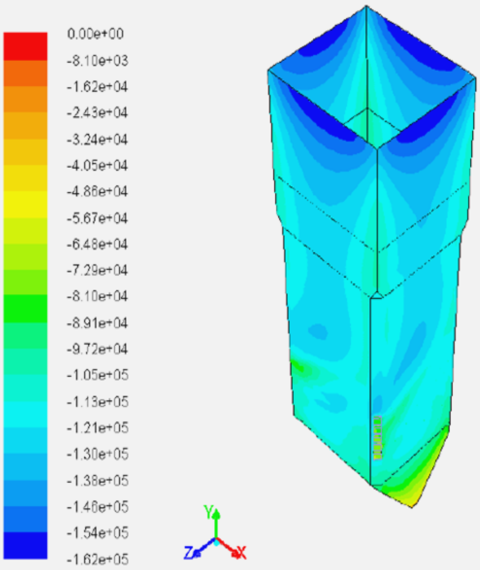

Fig. 4 Surface heat flux (W/m^2)

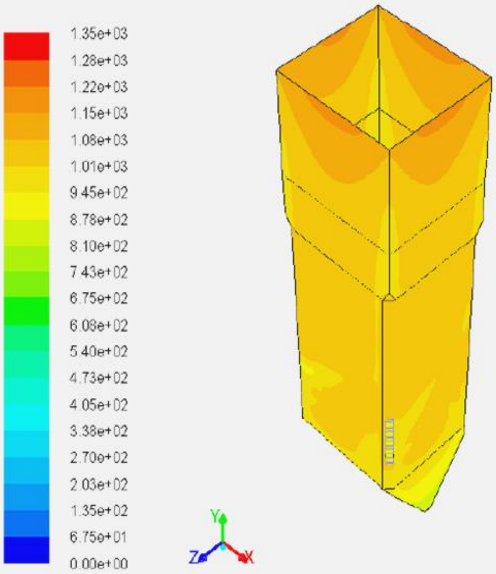

Fig. 5 Wall temperature inside boiler (K)

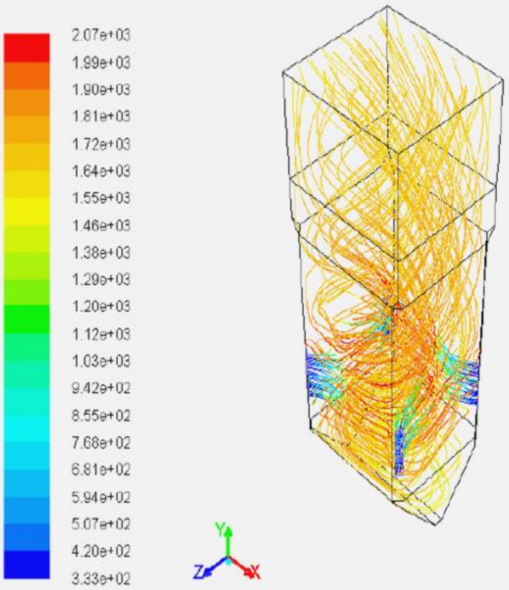

Fig. 6 Particle trajectory and temperature (K)

IV. CONCLUSION

The equilibrium and phase diagram models were found to be useful in identifying composition of slag and predicting ash fusion temperature. The CFD simulation results of gas temperature distribution, particle temperature and trajectory showed possibility of slagging deposition. The results of FactSage program may be used to compare with subsequent slag and ash fusion temperature experiments.

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Physical Characterization of Slag from Combustion of Lignite with High Ca Content

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Abstract

Mae Moh power plant produces electricity from pulverized coal combustion system. It has 10 units, generating electricity at about 18,000 GWh per year. At present, sometime the plant has been experiencing slag problem due to high calcium content in lignite used. At high load operation, excessive slag accumulation on the boiler walls may occur, possibly causing outage or derating. In this work, samples of boiler slag from Mae Moh power plant were collected and analyzed. Scanning electron microscopy analysis of the boiler slag showed that the majority of the crystal surface was agglomerates of particle-like clay and irregular granules stack together. Energy dispersive X-ray spectroscopy analysis showed that the main elements of slag were O, Si, Ca, Al and Fe, which can be included as SiO_2, CaO, Al_2O_3 and Fe_2O_3 in lignite ash. Ash fusion temperature (AFT) of the boiler slag was also analyzed for ash fusibility against ash composition. Initial deformation temperature was found to increase with increasing SiO_2 and Al_2O_3, but decrease with increasing CaO. For interaction effect, increasing ratio of base/acid was found to reduce AFT. Slag problem was directly related to low AFT of the ash. It was evident that high CaO in the lignite used resulted in increased intensity of slag.

Keywords: slag, lignite, ash deposit, pulverized coal combustion, Mae Moh, power generation

1. Introduction

Mae Moh power plant is a pulverized coal-fired power plant, with total capacity of 2,400 MW. The 10 units can supply power to approximately 18,000 GWh per year, representing 28.3% of total electricity production from Electricity Generating Authority of Thailand. Process of electricity generation is shown in Figure 1. Mae Moh lignite mine, with production of about 15-17 million tons per year supplies feedstock for the power plant.

Each region of the mine produces different characteristics of lignite. So blending management is required to meet the power plant input fuel specification. The typical chemical compositions of the lignite are shown in Table 1. The mixed coal must have sufficiently high heating value, under limitation of %sulfur, and calcium oxide in ash (CaO free SO_3) must not exceed 23% [1-2]. The value has been estimated to cause melting of ash. Assessment of the quality of coal found in the remaining areas revealed that coal with up to 40% CaO

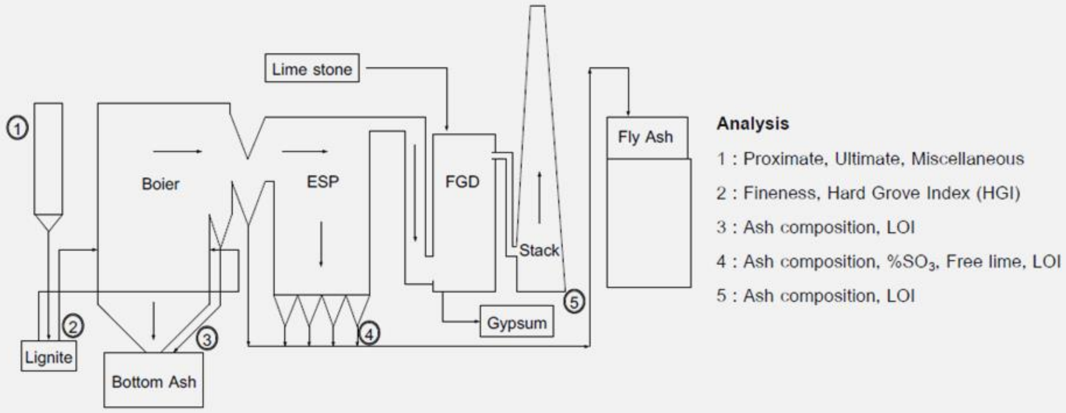

Fig. 1. Process of Mae Moh power plant and routine analysis

Table 1 Properties of Mae Moh lignite

Properties		Max.	Min.	Avg.
Proximate analysis (%w/w as-received basis)	Moisture (%)	34.38	30.71	32.28
	Volatile matter (%)	41.86	37.65	39.25
	Fixed carbon (%)	16.63	13.84	14.98
	Ash (%)	28.53	22.19	26.18
Heating value (%w/w dry basis)	HHV (MJ/kg)	18.30	15.68	16.78
	LHV (MJ/kg)	17.61	15.00	16.10
Ultimate analysis (%w/w dry basis)	Carbon (%)	48.94	45.29	46.73
	Hydrogen (%)	3.08	2.54	2.83
	Nitrogen (%)	1.81	1.59	1.71
	Oxygen (%)	12.90	11.95	12.44
	Sulfur (%)	4.11	3.60	3.96

may be available in the future. It has been proved that more frequent and severe slagging problems such as loss of capacity, loss of heat, boiler equipment damage, loss of time and money in maintenance boiler will occur.

In a boiler chamber, organic material in coal is combusted under high temperature and high pressure conditions. Mineral matter transforms into ash [3], as shown in Figure 2. The ash particles adhere to the surface of the slag sinter layer, and then melt into liquid and transform to solid slag on furnace walls or other surfaces exposed predominately to radiant heat or excessively high gas temperatures [4]. Slag is caused by many factors, such as coal organic properties, coal mineral matter properties, mineral transformation and decomposition, fluid dynamics, ash transport phenomena, vaporization and condensation of ash species, deposit chemistry-specie migration and reaction and heat transfer to and from the deposit [5]. To understand slag problem, investigation on slag characteristics and properties is required.

In this work, samples of boiler slag from Mae Moh power plant operated on lignite with high Ca content, were collected and analyzed qualitatively and quantitatively. Analysis of ash properties were carried out to assess slag problem.

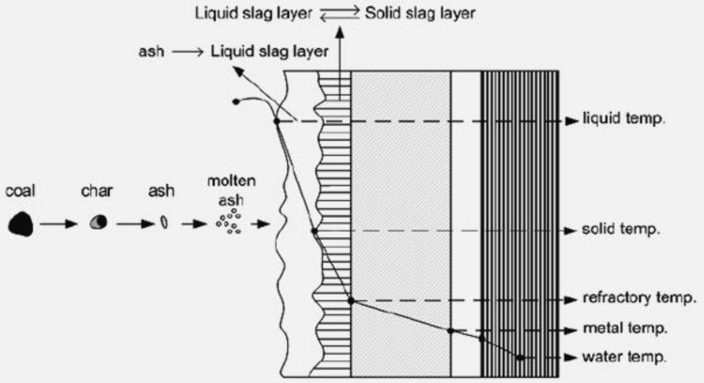

Fig. 2. Slag deposit formation [4]

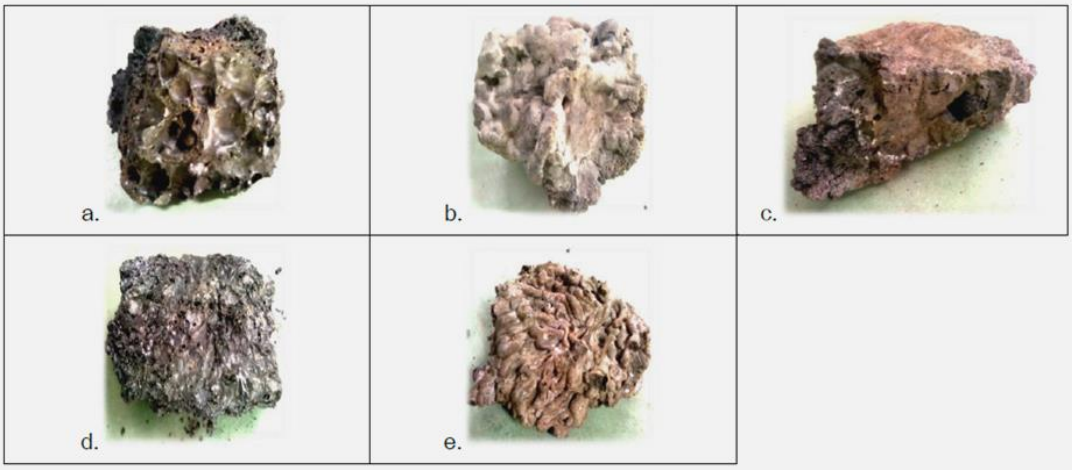

Fig. 3. Slag samples from the combustion of lignite with high Ca content : (a) dark brown to black with a shiny surface, riddled with small and large the same (b) brown like cement, large but fragile (c) brown with a small hole, hard but brittle (d) black and glossy, fall easily into small crystals and on the other side of slag like the boiler wall (e) brown, like a fusion of lava, full of holes, crystals contain a large amount of sand to fall.

2. Methodology

2.1 SEM-EDS measurements

Slag samples from the combustion of lignite with high Ca content with different appearances (Figure 3) were collected for analysis with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). SEM –EDS were used to describe the microstructural feature and chemical composition in slag deposition [6-9]. The samples were prepared, dried, sized to no larger than 3 mm. Their top surfaces were coated with gold to conduct electricity for analysis on a low vacuum scanning electron microscope JEOL JSM-5910LV at 15 kV and EDS.

2.2 Data analysis

The data from SEM-EDS were compared with those from the X-ray fluorescence spectrometry (ASTM D4326) from Mae Moh power plant. The main ash composition in the slag were Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, SO_3, K_2O, CaO, TiO_2, Fe_2O_3 and MnO_2 [1- 12]. Evaluation of the deposition behavior based on base to acid ratio (B/A) was calculated from Eq. (1) [1, 4, 11-12]. B/A ratio is an indication of the fusion characteristics and slagging potential of coal ash, ash-containing metals to combine in the combustion process to produce low melting salts.

$$\frac{B}{A}=\frac{Fe_2O+CaO+MgO+Na_2O+K_2O}{SiO_2+Al_2O_3+TiO_2} \qquad (1)$$

Ash flow temperatures (AFT) were analyzed following ash fusibility standard (ASTM D1857-04). It is a property that gives an indication of ash agglomeration and ash clinkering during combustion, in line with the tendency of ash to slag [3]. AFT consists of four temperatures, initial deformation temperature (IT), softening temperature (ST), hemispherical temperature (HT) and fluid temperature (FT) [4]. The ash composition and B/A ratio were used as parameters for correlating ash fusibility with its composition.

3. Results and Discussion

3.1 Surface morphologies and element compositions

SEM was used to examine the surface morphologies of slag. Element identification analyses of the samples were obtained by EDS. The results of the SEM images and elemental compositions of slag are presented in Figure 4. Although the appearances of the collected slag were different, the characteristics of the surface of the SEM analysis with a random two 2-piece indicated that they were not different. The majority of the crystal surface were agglomerates of particle-like clay and irregular granules stack together. The slag was found to be abundance of oxygen, aluminum, silica and calcium, which were probably quartz (SiO_2) [2, 8-9, 13], anorthite ($CaAl_2Si_2O_8$) [7, 10], mullite ($Al_6Si_2O_{13}$) [10], gehlenite ($Ca_2Al_2SiO_7$) [10], kaolinite ($Al_2Si_2O_7$) [7, 10, 13] and calcium oxide (CaO) [14]. Quartz and kaolinite are major mineral phases of coal during combustion in a large power station, and quartz, mullite and calcium oxide are major inorganic phases in slag [14] .The chemical reaction during the combustion of mullite and calcium oxide produces anorthite at 950°C. The reaction between anorthite and calcium oxide is gehlenite, according to Eqs. (2) and (3) [10].

$$mullite\ \ (Al_6Si_2O_{13})+calcium\ \ oxide\ \ (CaO) \xrightarrow{950^{\circ}C} anorthite\ \ (CaAl_2Si_2O_8) \qquad (2)$$

$$anorthite\ (CaAl_2Si_2O_8)+calcium\ \ oxide\,(CaO) \rightarrow gehlenite\ \ (Ca_2Al_2SiO_7) \qquad (3)$$

Carbon, iron, magnesium and potassium were also found. These are calcite ($CaCO_3$) [7-9], dolomite ($CaMg(CO_3)_2$) [8], ankerite ($cafe(CO_3)$) [9], iron alumino-sillicate ($FeO+SiO_2+Al_2O_3$) [10, 13] and siderite ($FeCO_3$) [9, 11, 12, 15]. Inorganic elements, Ca, Na and Mg, dissolved salts in the pore waters of coal may have lower melting points [10]. The slag samples were analyzed for physical properties similar to previous studies, and related to the chemical elements that affect the slag.

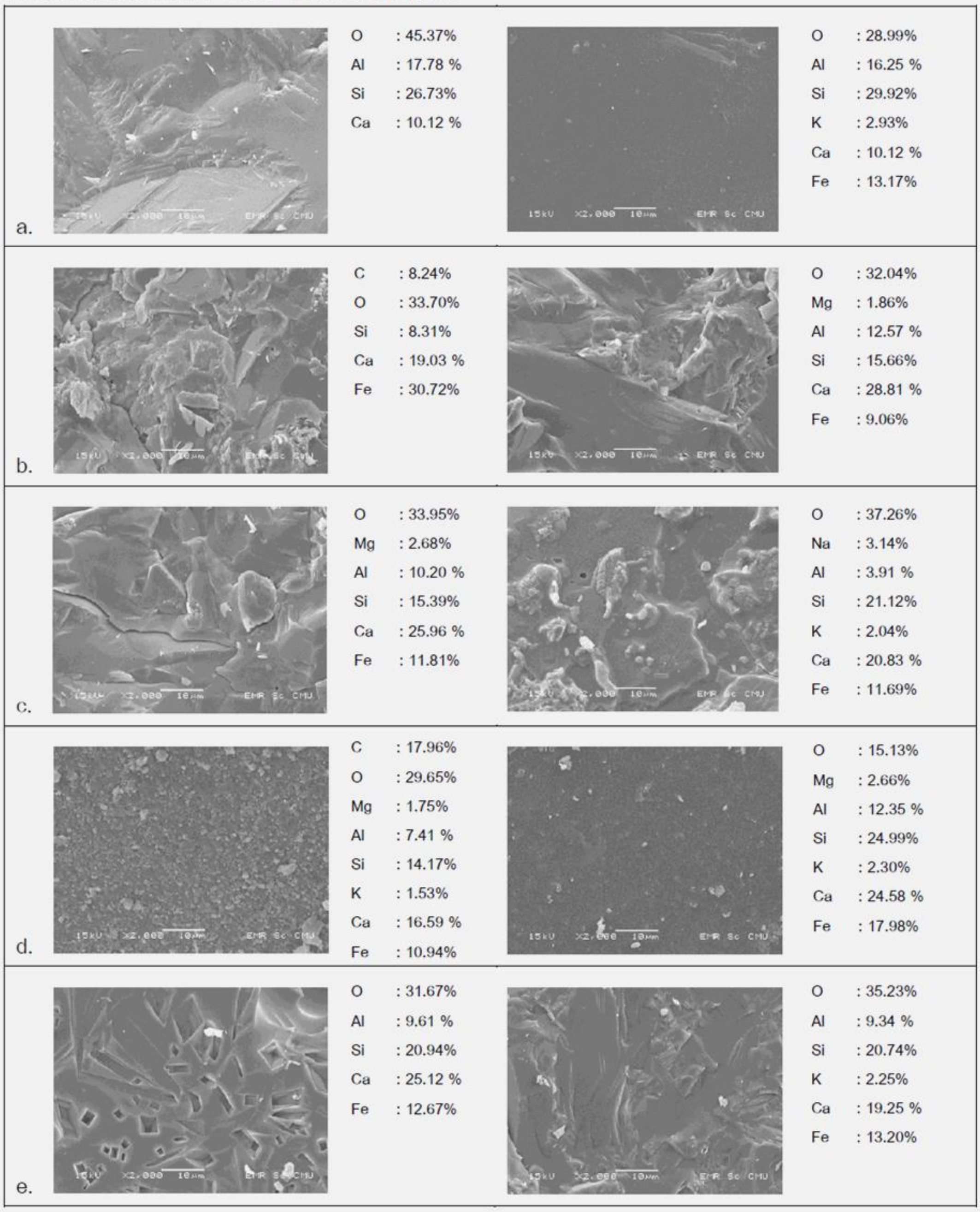

Fig. 4. surface morphologies and elemental compositions of slag

3.2 Relationship between ash chemistry and ash fusibility

The lignite ash composition from X-ray fluorescence spectrometer is shown in Table 2. It can be seen that the major elements in ash were in combination of Al_2O_3, SiO_2, SO_3, Fe_2O_3 and CaO, accounting for about 80%. This is consistent with the elemental analysis of slag by EDS, where there are O, Si, Ca, Al and Fe.

Therefore, the relationship of the SiO_2, CaO, Al_2O_3, and Fe_2O_3 affected the initial deformation temperature (IT) [2, 9], as shown ternary diagram in Figures 4 and 5. Both contours clearly suggest that the amount of CaO added resulted in decreased IT. While Fe_2O_3 increased, IT slightly decreased. This was in contrast to Si and Al. This was consistent with previous research that CaO and Fe_2O_3 were very effective fluxes for aluminosilicates, giving rise to sticky ash particles and lowering the melting point of the ash. Increasing Al_2O_3 and SiO_2 generally rised the IT [2].

Table 2 Lignite ash composition during combustion of lignite with high Ca content

Element	wt% in ash
Na_2O	0.36-0.81
MgO	1.84-2.42
Al_2O_3	11.90-16.62
SiO_2	22.95-30.66
P_2O_5	0.16-0.22
SO_3	18.16-25.20
K_2O	1.47-2.14
TiO_2	0.24-0.36
Fe_2O_3	12.33-14.14
MnO_2	0.12-0.16
CaO	15.63-21.97

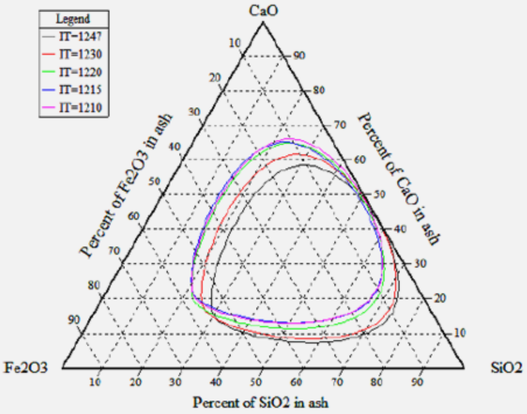

Fig.4. Ternary diagram of CaO-SiO_2-Fe_2O_3 system.

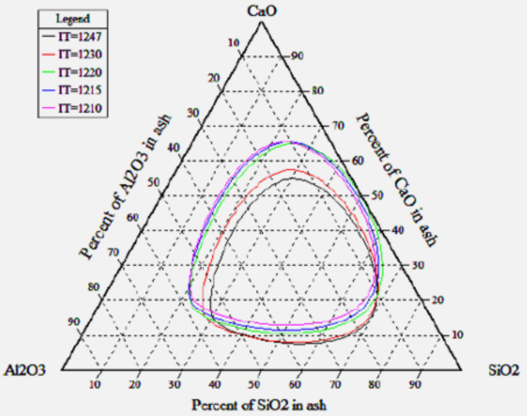

Fig.5. Ternary diagram of CaO-SiO_2-Al_2O_3 system.

The calculated B/A ratios were plotted against AFT, shown in Figure 6. It was observed that when the B/A ratios increased, AFT decreased. This was consistent with previous research, which shows that B/A ratios below 0.2 are likely to be low deposition, a value between 0.2-1.0 is medium deposition tendency, and values greater than 1.0 indicates that the potential is high [12]. McLennan [11] used to find the slagging potential of the B/A ratio. The increase of % sulfur in dry coal is proportional to base oxide, which defines that the lower range of the slag is less than 0.6, the medium is in range of 0.6-2.0, high is 2.0-2.6 range, respectively. If %sulfur is greater than 2.6, it can cause severe slag. Mae Moh case was greater than 2.6, which is severe.

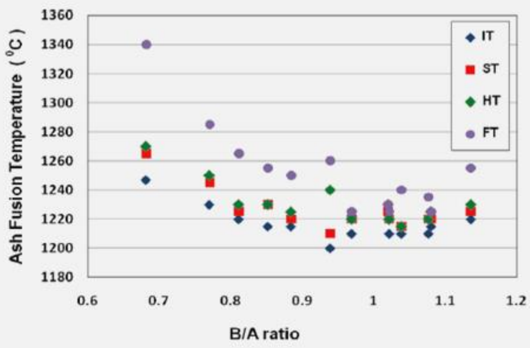

Fig. 6. Ash fusion temperature as a function of B/A ratio from combustion of lignite with high Ca content

4. Conclusions

In the present study, physical characterization of slag from combustion of lignite with high Ca content in Mae Moh power plant was carried out. Slag samples from a boiler were taken. The appearances were observed to be different. Having analyzed by SEM and EDS, it was indicated that the surface morphologies of slag were similar. The majority of the crystal surface was agglomerates of particle-like clay and irregular granules stack together. Elements in the slag were found to be abundance of oxygen, aluminum, silica and calcium, which were probably quartz, anorthite, mullite, gehlenite, kaolinite and calcium oxide. Consistent with the results of X-ray Spectroscopy analysis of the ash composition, they were SiO_2, CaO, Al_2O_3 and Fe_2O_3 as the main components. The relationship between SiO_2, CaO, Al_2O_3, and Fe_2O_3 was found to affect IT. IT was found to increase with increasing SiO_2 and Al_2O_3, but decrease with increasing CaO. For interaction effect, increasing B/A ratio was found to reduce AFT. It was indicated that the slagging potential was high and severe. CaO in lignite affected slagging significantly.

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