Effect of Coal Blending on Ash Fouling and Slagging in Pulverized Coal-Fired Supercritical (SC) and Ultra-Supercritical (USC) Power Plants

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Bachelor of Engineering

This thesis is presented for the Degree of Doctor of Philosophy of The University of Western Australia

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Declaration

I hereby certify that the work embodied in this thesis is the result of my original research under the supervision of Professor Dongke Zhang and co-supervisor Dr Mingming Zhu, and has not been submitted for a higher degree to any other University or Institution.

Nonetheless, some of the original research results have been published in journals or conference proceedings for recognition of our work. Please see the publications section in this thesis.

Signature: ________________________
(JIANBO LI)

Date: 21-11-2016
To My Beloved Family
Abstract

This thesis research was aimed to investigate the effect of coal blending on ash fouling and slagging during combustion in pulverised coal-fired supercritical (SC) and ultra-supercritical (USC) boilers. Particular attention was paid to ash deposition mechanisms and deposit behaviour during the combustion of Zhundong lignite of high alkali and alkali earth contents. An Australian bituminous (AB) and an Indonesian lignite (IL) with vastly different mineralogy and chemistry to those of the Zhundong lignite were also employed in this work. Through a systematic study of the characteristics of coal mineral matter and inorganic constituents, ash prepared from combustion in a muffle furnace, and ash deposits formed on a probe in a drop tube furnace simulating superheaters in subcritical, supercritical and ultra-supercritical boilers, this research provided an improved understanding of the effect of probe temperature on ash deposition, ash deposition mechanisms and deposit behaviour of the Zhundong lignite, and the coal blending effect as a potential mitigation strategy for ash deposition of Zhundong lignite.

The effect of coal blending on the ash sintering temperature, fusion temperatures and mineral transformation during the combustion of Zhundong lignite (ZL) in a muffle furnace operating at 815 °C in air was investigated. The results showed that the ZL ash was rich in basic oxides with Ca-bearing minerals anhydrite, calcium silicate and yeelimite being dominant, incurring relatively low ash sintering and fusion temperatures. In contrast, both Australian bituminous (AB) and Indonesian lignite (IL) coal ashes were rich in acidic oxides in the forms of refractory mineral such as quartz, leading to relatively high ash sintering and fusion temperatures. As the AB or IL ratio in the blends increased, the sintering temperature of the ash increased, indicating that the sintering tendency of the ash of the blend decreased. However, the softening temperature (ST) and fluid temperature (FT) of the ash firstly decreased as the AB or IL addition ratio increased, and then increased afterwards, indicating that the AB or IL coal ash of high melting-points would not increase the ash fusion temperatures above a certain blending ratio. The significant variation in the chemistry and mineralogy of the ash as a result of coal blending and mineralogical interactions was the main reason for the changes to the ash sintering and fusion characteristics.
The effect of coal blending and probe temperature on the ash deposition was also studied through the analysis of the deposits formed on an air-cooled probe at different temperatures during the combustion of Zhundong lignite in a drop tube furnace. At the probe temperature of 500 °C, the ZL ash deposit was dominated by fluxing minerals where significant amounts of fine particles (< 10 μm) and their aggregates existed, leading to low ash sintering temperatures. As the AB ratio increased to 20wt% and above, the amount of the fluxing minerals in the deposits decreased while the amount of refractory quartz and mullite minerals increased. Morphologically, the refractory ash particles from AB coal inhibited the formation of Na- bearing mineral phases and reduced the contacts between fine ash particles, leading to the absence of nepheline and, correspondingly, an increase in the ash sintering temperature. Similarly, the addition of IL into ZL increased the ash sintering temperature of the blend, diluted the fine fluxing ash particles, and therefore mitigated ash deposition. In addition, as the probe temperature was increased from 500 °C to 750 °C, mineral interactions and ash sintering were facilitated when the AB ratio was less than 20wt%, leading to the formation of hauyne and an increase in particle sizes. However, these changes were not observed when the AB ratio was higher than 40wt%, indicating that these ash deposits were more refractory and resistant to the temperature change.

The effect of coal blending, addition of additives and water washing on the structural stratification and chemistry of the Zhundong lignite ash deposits was also investigated. Results showed that fine lime, anhydrite, and hematite ash particles initiated ZL ash deposition with calcium sulphation reaction occurring on the probe. Blending AB or IL into ZL introduced more refractory ash particles, diluted the fine ash particles, and therefore mitigated the ZL ash deposition. In addition, a similar mitigation effect on the ash deposition was found when kaolin or bauxite was added into ZL. However, the ash stratification and chemistry of ZL and water washed ZL did not show significant differences according to SEM-EDS analysis, suggesting that its effectiveness in ash deposition mitigation warrants further quantitatively investigation.
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Publications in Conference Proceedings


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Figure 8-2  A schematic representation of the deposition mechanisms and processes of the main mineral phases during the combustion of Zhundong lignite
Coal is an important energy source for raising steam and generating electricity, which plays a pivotal role in supporting modern life and industry (Zhang 2013). However, as coal is a combustible rock and consists of complex organic and inorganic matter (Zhang 2013), the generation of ash residues is inevitable during the burning of coal. During the combustion in pulverized coal-fired boilers, the generated ash, apart from leaving the boilers as fly ash and bottom ash, would also deposit on the heat transfer surfaces and stay in the boiler. Ash deposition on these heat transfer surfaces will reduce the heat transfer efficiency, increase the thermal input requirement, and in extreme cases, lead to unscheduled outage of the plant (Raask 1985; Baxter 2000; Zhang 2013).

The scientific principles of ash deposition are related to the mineral matter in coal, the operating conditions and the boiler design (Bryers 1996; Zhang 2013). Mineral matter in coal, being the sum of all discrete inorganic minerals and organically-bound inorganic elements, is the culprit for ash deposition. The common mineral matter in coal that contributes significantly to ash deposition includes Si, Al, Ti, Fe, Ca, Mg, Na, K, S and Cl (Bryers 1996). However, the concentration and mode of occurrence of the mineral matter in coal are dependent on coal rank and region (Vassilev et al. 1994; Vassilev et al. 1996; Vassilev et al. 1997; Vassilev et al. 2000). High rank coal is often rich in Si and Al and tends to have less ash deposition problem, while the low rank coal on the contrary is more prone to cause severe ash deposition due to its abundant iron or alkali and alkali earth contents (Xu et al. 2013; Zhou et al. 2013). In an effort to manage and mitigate ash deposition during combustion of low rank coal, coal blending has been extensively employed in practical power plants (Raask 1985; Su et al. 2001; Rubiera et al. 2002; Su et al. 2003; Wang et al. 2008; Wang et al. 2009; Tillman et al. 2012). However, the effect of coal blending on ash deposition, depending on the mineral matter in coal and the blending ratio, is diverse and unpredictable. Coal blending may mitigate ash deposition, but in some cases would also aggravate ash deposition due to the mineral interactions. Therefore, understanding the effect of coal blending on mineral transformation and ash deposition during combustion of low rank coal is essential to extend its utilisation.
Chapter 1 Introduction

The operating conditions and boiler design including boiler load, air to fuel ratio, gas temperature, soot blowing patterns, and of particular concern the heat transfer surface temperature are also responsible for ash deposition (Bryers 1996; Zhang 2013). In the pursuit of higher efficiency for electricity generation, more supercritical (SC) and ultra-supercritical (USC) power plants are developed or being developed currently. Under these circumstances, the temperature of steam is increased which in turn elevates the temperature of the heat transfer (mainly superheaters) surface. In these cases, the ash deposition mechanisms and deposit behaviour in SC and USC boilers on higher surface temperatures may differ from those in subcritical boilers.

Taking the aforementioned aspects into consideration, this study is scoped to investigate the effect of coal blending on ash deposition (fouling and slagging) in pulverized coal-fired supercritical (SC) and ultra-supercritical (USC) power plants. Three types of coal namely, Zhundong lignite, Indonesian lignite, and Australian bituminous with vastly different geochemistry and ash mineralogy are chosen for the preparation of coal blends. The mineral transformation, sintering and fusibility characteristics of ash samples prepared in muffle furnace are investigated, and the ash deposits formed on a probe at different temperatures simulating superheater surfaces in subcritical, supercritical and ultra-supercritical boilers are collected and characterised with the blending effect investigated. Particular attention is given to the ash deposition behaviour and mechanisms during the combustion of Zhundong lignite due to its severe ash deposition problem yet insufficient investigation in the literature (Zhou et al. 2010; Xu et al. 2013).

The overall aims of this study are to investigate:

- How minerals and mineral matter in coal blends interact during combustion;
- How and why coal blending can mitigate (or aggravate) ash fouling and slagging;
- How ash deposition differs in subcritical, supercritical, and ultra-supercritical boilers.
- Devise strategies to mitigate ash deposition of Zhundong lignite.

The structure of this thesis is graphically presented in Figure 1-1. There are a total of nine chapters as follows:

- The present chapter (Chapter 1) defines the scope and the overall aims of the thesis as well as the thesis structure;
Chapter 1 Introduction

- Chapter 2 reviews the current understandings of the mineral transformation, the methodology of ash characterisation, the mechanisms of ash deposition and deposit development, and the mitigation strategies for ash deposition. The existing gaps in this field are identified and the specific objectives of the thesis are developed;
- Chapter 3 presents the research methodology, the materials, the experimental equipment and analytical instruments that are used in the thesis;
- Chapter 4 characterises the mineralogy, chemistry, fusibility, and sintering temperatures of the ash samples generated from muffle furnace during combustion. The effect of coal blending on these characteristics as well as on mineral transformations is analysed;
- Chapter 5 investigates the ash deposition on a probe at probe temperature of 500 °C in a drop tube furnace simulating the ash deposition in subcritical boilers during combustion of coal blends. The mineralogy, morphology and sintering temperature of the deposited ash samples are analysed, and the effect of coal blending on these characteristics and on the deposition mechanisms is discussed;
- Chapter 6 simulates the ash deposition in supercritical and ultra-supercritical boilers after increasing the probe temperature to 600 °C, 700 °C and 750 °C. The effect of probe temperature on the mineralogy, morphology and sintering temperature of the deposits is discussed;
- Chapter 7 focuses on the effect of time, probe temperature, coal blending, water washing, and additives on the structure and chemistry of the deposits, shedding lights on the ash deposition mechanisms and mitigation strategies for ash deposition of Zhundong lignite;
- Chapter 8 analyses and evaluates the experimental results, integrates the findings, and discusses the implications of the present study for ash deposition in the practical applications and in further scientific studies;
- Chapter 9 concludes the thesis with major new and significant findings from this study, and provides several considered recommendations for future work.
1 Introduction
- Define the Scope
  Effect of coal blending on ash fouling and slagging in pulverized coal-fired SC/USC power plants
  - Aims and Structures
  How ash deposition differs in sub-critical, SC, and USC boilers;
  How blends can mitigate or aggravate slagging and fouling;
  How coal minerals interact in blending.

2 Literature Review
- What has been done? Slagging and fouling of coal and coal blends; mineral transformation etc.
- How did they do? Analysis of ash and deposits properties; deposition rate etc.
- What has been learnt? Deposition, initiation, processes and mechanisms; mineral interactions;
- What has not or less been done? Deposition in SC/USC boilers; Coal blending effect on Zhundong lignite ash deposition

3 Methodology and experimental approach
- Coal samples
  Zhundong lignite, Australian bituminous, Indonesian lignite, and their blends
  - Ash preparation: Plasma, muffle
  - Ash deposition probe
  - Ash analysis
  AFTs, Ts, XRD, SEM/EDS, ICP
  - Deposit preparation and analysis
  DTF, analysis of deposit layers

5 Blending effect on fouling and slagging in SC/USC boilers
- DTF with probe at 600 °C, 700 °C, and 750 °C;
- Deposit analysis (SEM-EDS, XRD, Ts)
- Evaluation of different blends

6 Blending effect on fouling and slagging in subcritical boilers
- DTF with probe at 500 °C
- Ash sample analysis (SEM-EDS, XRD, Ts)
- Evaluation of different blends

4 Characterization of coal ashes of blends from muffle furnace
- Ash preparation
- Ash fusibility (AFTs)
- Sintering characteristics (Ts)
- Mineral identification, transformation and interaction
- Implication for slagging and fouling

7 Structure and chemistry of Zhundong lignite ash deposits
- Coal blending, water washing and additives
- Analysis of the deposit layers (SEM-EDS, Ts)
- Evaluate the different methods

8 Integration, evaluations and applications
- Integration of the coal blending effect
- Integration of the probe temperature effect
- Evaluation of the results and errors
- Implications for practical use

9 Conclusions and Recommendations
- Why coal blends can mitigate/aggravate the problems
- How can we guide coal blending
- How water washing and additives affect slagging and fouling of Zhundong lignite
- How minerals interact; which minerals/eutectics responsible for slagging and fouling

Figure 1-1 Thesis map
2.1 Background
Ash deposition on heat transfer surfaces, although has been investigated for many decades, remains to be a troublesome problem in pulverized coal-fired boilers (Raask 1985; Bryers 1996; Baxter 2000; Zhang 2013). During combustion in pulverised coal-fired boilers, approximate 10%-30% of the generated ash will deposit within the furnace, primarily in the hoppers at the bottom of the furnace, but also on the interior surfaces, leading to the formation of ash slags (Hurley et al. 1998). The remaining ash leaves the boiler with the flue gas but still has chance to deposit on steam tubes as fouling deposits (Hurley et al. 1998). A schematic diagram of the fate of the generated ash in pulverised coal-fired boilers is shown in Figure 2-1 (Fernandez-Turiel et al. 2004). These ash deposits on the heat transfer surfaces increase the thermal resistance of the heat transfer surfaces, decrease the thermal efficiency of the plant, and in some cases lead to plant outages (Raask 1985; Zbogar et al. 2005). Economically, ash deposits resulted in an annual cost of over $1.2 billion in the US coal-fired power generation market from 1995 to 2004 (Harding et al. 2007). The economic impact of ash deposition would be even greater if worldwide power generation market is taken into consideration. Therefore, understanding the ash deposition mechanisms, deposit behaviour and properties, and developing mitigation strategies for ash deposition during pf combustion are still imperative to extend the use of certain coals and maintain stable operation of the power plants.

Attributable to the significant practical impacts of ash deposition and the scientific interests arising from it, there has been a large volume of literature, of accumulated academic research and engineering experiences, on ash formation, deposition, and deposit characteristics of different coals worldwide (Bryers 1996; Vuthaluru et al. 1998; Vuthaluru et al. 1999; Vuthaluru et al. 1999; Vuthaluru et al. 2000; Telfer et al. 2001; Vuthaluru et al. 2001; Vuthaluru et al. 2001; Yan et al. 2001; Li et al. 2004; Pipatmanomai et al. 2009; Chen et al. 2012; Luan et al. 2014; Luan et al. 2014; Wang et al. 2014; Li et al. 2016; Li et al. 2016). However, ash deposition is determined by the mineral matter in coal, the operating conditions and the boiler design, exhibiting diverse ash deposition behaviours due to a suite of deposition mechanisms. Mineral matter in
coal is the culprit for ash deposition, while the operating conditions and the boiler design determine the fates of the mineral matter during combustion, how the generated ash are deposited, and how the structure and strength of the deposit are developed.

![Diagram of a pulverised coal-fired furnace and the fates of the ash generated during combustion](image)

**Figure 2-1** A schematic diagram of the pulverised coal-fired furnace and the fates of the ash generated during combustion (Reproduced from Fernandez-Turiel et al. 2004)

To gain a better understanding of the ash deposition problem during combustion in pulverised coal-fired boilers, this chapter reviews the literature research on the mineral matter in coal, mineral matter transformation and interactions during combustion, the methodology of ash characterisation, the mechanisms of ash deposition, the deposit structure and strength development, and the mitigation strategies for ash deposition. Based on the literature review, the existing gaps in this field are identified, and the objectives of the current research are developed.

### 2.2 Mineral matter in coal

Coal is a heterogeneous mixture of organic and inorganic constituents in the forms of compulsory solid, liquid and gaseous phases (Vassilev et al. 2001). During combustion of coal, the organic constituents will be burnt and at the same time release energy. While the inorganic constituents are regarded as mineral matter in the coal and will eventually form ash after the coal is burnt.
Mineral matter in coal is the non-combustible portion of the components present in coal and is generally considered to be the sum of all discrete inorganic mineral phases and organically-bound inorganic elements (Bryers 1996). There are at least 11 inorganic elements with significant concentrations present in coal and contribute to ash deposition during combustion: Si, Al, Fe, Mg, Ca, Na, K, Ti, P, S, and Cl (Bryers 1996). Depending on their associations with the carbonaceous portion of coal, the mineral matter in coal can be classified into minerals (excluded and included minerals) and organically-bound (or organically-associated) inorganic elements as illustrated in Figure 2-2 (Raask 1985; Bryers 1996). Excluded minerals are free of the carbonaceous portion and can be readily separated by physical methods (Raask 1985; Bryers 1996; Rushdi et al. 2004; Ngee 2008). While included minerals and organically-bound elements are bonded in coal matrix and intimately associated with the carbonaceous portion of coal, which usually can’t be readily separated by general physical methods.

Figure 2-2  The classification of the mineral matter in coal and its association with coal matrix (Reproduced from Raask 1985)

Minerals
Mineral is the predominant form of the inorganic elements in coal (Zhang 2013). More than 125 minerals have been identified in coal or low temperature coal ash (Klein et al. 1993; Vassilev et al. 1994; Vassilev et al. 1996; Vassilev et al. 1996; Vassilev et al. 1997; Vassilev et al. 1997; Vassilev et al. 2000; Vassilev et al. 2001). These minerals include silicates, oxyhydroxides, sulphates, carbonates, sulphides, phosphates, chlorides, and other mineral species. The mode of occurrence (minerals and phases), morphologies, size distribution, origin, and abundance of these minerals are summarised in Appendix I (Klein et al. 1993; Vassilev et al. 1994; Vassilev et al. 1996; Vassilev et al. 1996; Vassilev et al. 1997; Vassilev et al. 1997; Vassilev et al. 2000; Gupta et al. 1998; Vassilev et al. 2000;
Generally, the approximate quantitative distribution of these groups in descending order is (Bryers 1996; Wee et al. 2005; Wee et al. 2006):
Silicates > Carbonates > Oxyhydroxides > Sulphides > Sulphates > Phosphates > Others

Among these minerals, the major minerals commonly include quartz, kaolinite, illite, feldspars, calcite, pyrite, and gypsum (Raask 1985). The minor minerals are usually cristobalite, montmorillonite, mica, chloride, zeolites, hematite, goethite, diaspore, brucite, barytocalcite, dolomite, siderite, marcasite, jarosite, alunite, hexahydrite, barite, and apatite. The other minerals identified were commonly in accessory and trace concentration (Vassilev et al. 1995).

The composition and proportion of these minerals are greatly dependent on coal rank and region (Klein et al. 1993; Vassilev et al. 1996; Vassilev et al. 1996). High rank coal is usually rich in quartz, kaolinite, illite, mica, chloride, spinel, dolomite, siderite, hexahydrite, and Fe oxyhydroxides, leading to higher contents of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, and TiO$_2$, but has a decreasing trend of montmorillonite, feldspars, zeolite, Al oxyhydroxides, calcite, pyrite, gypsum and Fe, Al and Ba sulphates (Vassilev et al. 1996). Low rank coal, however, is usually rich in calcite, pyrite, gypsum, and other sulphates, leading to higher contents of MgO, CaO and SO$_3$ (Vassilev et al. 1996). In addition, the composition and proportion of minerals are also dependent on coal region, leading to vastly different mineral phases in coal from different origins or seams (Klein et al. 1993; Vassilev et al. 1996). As a consequence, coal is very heterogeneous in nature and the above trends in literature may not be applied to one typical coal. Therefore, characterisation of the minerals and mineral matter in coal is the fundamental step to understand the ash and their deposition characteristics.

**Organically-bound inorganic elements**
The mineral matter in coal can also be organically bounded with the carbonaceous portion of coal. The common organically-bound elements in the coal include Na, Ca, and Mg. The composition and proportion of the organically-bound elements are also dependent on coal rank and region. Generally, the contents of organically-bound elements are depleted in high rank coal, but are abundant in low rank coal (Zhang 2013).
Chapter 2 Literature Review

Chemical fractionation technique

Chemical fractionation technique is recently applied to specifically determine the forms and the mobility of the mineral matter in aqueous or acid solutions (Said et al.; Baxter 2000; Arvelakis et al. 2001; Arvelakis et al. 2002; Yu et al. 2014). This process consists of three successive extractions. Water washing is the first step, which is to characterise the forms and mobility of the water-soluble elements including Na, Ca and Cl. The second extraction is ammonium acetate washing, which is to characterise the organically-bound elements such as Na, Ca, and Mg. The third extraction uses hydrochloric acid to characterise the acid-soluble species such as alkaline earth sulphates, and carbonates etc., and the residual material typically consists of insoluble silicates, oxides, and sulphides. Generally speaking, a high rank coal is depleted in water-soluble and acid-soluble mineral matter, while a low rank coal tends to enrich in water-soluble or acid-soluble inorganic constituents (Jenkins et al. 1996; Vuthaluru et al. 1999; Vuthaluru et al. 1999). During combustion, these mineral matter in different forms may experience different geochemical and mineralogical transformations at high temperature, and therefore play different roles during ash deposition (Li et al. 2015).

Literature reviews into the mode of occurrence, size distribution, morphology, abundance and origin of the mineral matter have indicated the heterogeneous nature of coal, providing a rough but limited idea on the characteristics of the mineral matter in coal. Detailed analysis on the characteristics of mineral matter in a coal sample is still the first crucial step to identify the key ash forming species in coal during combustion.

2.3 Mineral matter transformation during coal combustion

During coal combustion at high temperatures, the mineral matter in coal undergoes complex mineral transformations and interactions, leading to new mineral phases that differ from its original mode of occurrence. The behaviours of the mineral matter at high temperatures are directly responsible for ash deposition. Thus, understanding the mineral transformations and interactions of the mineral matter subjecting to high temperature environment during combustion are essential for understanding ash deposition and deposit properties.

2.3.1 Transformation of minerals

The summary of the mineral phases in Appendix I shows that quartz, kaolinite, illite, calcite, siderite, and pyrite are common minerals that present in coal (Hurley et al.
Chapter 2 Literature Review

1992). Therefore, the transformation of these minerals, as references to comprehend the fates of silicates, carbonates, and sulphates at high temperatures, are discussed. The roles of these minerals on ash deposition are also reviewed.

**Quartz (SiO$_2$)**

Quartz is the most common mineral that is present in coal, which melts at 1723 °C and boils at 2230 °C (Bryers 1996). Excluded quartz is usually stable and retain its shape and structure during combustion (Raask 1985). As the temperature exceeds 950 °C, quartz will convert to other phases such as tridymite and cristobalite (Bryers 1996; Wee et al. 2005; Wee et al. 2006). Included silica often forms silica monoxide (SiO) in reducing atmosphere during combustion (Bryers 1996):

$$\text{SiO}_2 + \text{C} = \text{SiO}_{(g)} + \text{CO} \quad (R2.1)$$

The vapour pressure of SiO is usually very low, but it will be altered substantially once carbon and other mineral species are present. In the presence of pyrites or metallic iron, volatilization of included silica begins at about 1560 °C and continues until all the silica in the mineral is volatilized (Raask 1985; Bryers 1996). In addition, the silica monoxide will continue to react with oxygen and generate silica oxide (Tomeczek et al. 2002):

$$\text{SiO}_{2(g)} + \frac{1}{2} \text{O}_2 = \text{SiO}_{2(g)} \quad (R2.2)$$

These reactions can be well illustrated by the supersaturation mechanism based on the partial pressure and equilibrium pressure of SiO$_2$ (g). Silica fume is then formed after the re-condensation of SiO$_2$ (g) (Tomeczek et al. 2002). It is worth noting that this process is different from direct volatilisation-condensation process during combustion (ten Brink et al. 1997).

Quartz plays multiple roles during ash deposition. On one hand, quartz is able to absorb the condensed vapours, capture aggregates, and mitigate ash fouling (Bryers 1996). However, the formation of salicaceous particles (Na$_2$SiO$_3$) after absorption reaction would form low melting-points eutectics, leading to silica-induced slagging. Moreover, in the presence of potassium, more silicate glass can be formed at lower temperatures (Gupta et al. 1998).
Kaolinite (Al₂O₃·2SiO₂·2H₂O)

Kaolinite is the second major source of silica and is of great importance to ash behaviour. At the temperature of about 500 °C, kaolinite will dehydrate to amorphous metakaolinite, which will then form silicon spinel at about 925 °C. As temperature further increases to higher than 1100 °C or 1400 °C, mullite will be generated (Bryers 1996; Tomeczek et al. 2002; Wee et al. 2005; Wee et al. 2006):

\[
\begin{align*}
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} & \rightarrow 2\text{H}_2\text{O} + \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \quad (500 \sim 925 \degree C) \\
2(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) & \rightarrow \text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \quad (925 \sim 1100 \degree C) \\
2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 & \rightarrow \text{SiO}_2 \cdot 2(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2) \quad (>1100 \degree C) \\
3(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2) & \rightarrow 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + \text{SiO}_2 \quad (>1400 \degree C)
\end{align*}
\]

Similar to quartz, kaolinite can capture aggregates and act as an alkali absorbent (Bryers 1996). In addition, its high temperature mineral phase mullite is refractory and may not be completely liquid until about 1800 °C. Therefore, the greater the mullite or kaolinite content in the ash, the higher the ash fusion temperatures and the less propensity of ash fouling and slagging are expected (Huang et al. 2013).

Illite

Illite is another silicate but contains low concentration of potassium or sodium. Amorphous glass phase will be formed when the temperature reaches 950 °C. At temperature of 1100 °C, mullite will be formed (Bryers 1996; Tomeczek et al. 2002). In addition, the generated spinel can dissolve into glass when the temperature exceeds 1300°C. Illite is a fluxing agent which would decrease the ash fusion temperature and aggravate ash deposition (Bryers 1996).

Calcite (CaCO₃)

Calcite is one of the common carbonates and decomposes at low temperatures (ca. 810 °C) (Bryers 1996):

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 
\]

(R2.7)

In the presence of sulphate, interactions between lime and sulphur will occur, leading to the sulphation of calcium oxide:

\[
\begin{align*}
\text{CaO} + \text{SO}_3 & \rightarrow \text{CaSO}_4 \\
\text{CaO} + \frac{1}{2}\text{O}_2 + \text{SO}_2 & \rightarrow \text{CaSO}_4
\end{align*}
\]

(R2.8)  (R2.9)
Calcite is one fluxing mineral that enhances ash deposition. Excluded calcite may become sulphated at lower gas temperatures and form calcium-sulphate-bonded deposits, while included calcite could be one fluxing agent for other inherent minerals including aluminosilicate (Bryers 1996). The roles of included calcite and excluded calcite has not been well understood, even though there is no doubt about its fluxing property (Raask 1985; Ten Brink et al. 1995; Bryers 1996; Tomeczek et al. 2002).

**Siderite (FeCO₃)**

Siderite is one of the common carbonates that contain iron, which decomposes at the lowest decomposition temperature among carbonates, 585 °C. The forms of iron after decomposition includes Fe, FeO and Fe₃O₄, depending on the partial pressure of O₂, CO and CO₂ of the atmosphere (Bryers 1996).

Fe is problematic during ash deposition due to different reasons. Firstly, the reduced form of iron is adhesive and can be slagging initiators. Secondly, iron can also lower the melting point of aluminosilicate. And thirdly, iron in the slagging deposit will increase the stickiness of these metals (Bool Iii et al. 1995). Excluded siderite are less likely to induce ash related problems unless it contacts with other siliceous minerals on a hot surface, while included siderite acts as one fluxing agent for siliceous minerals (Bryers 1996).

**Pyrite (FeS₂)**

Pyrite is a combustible mineral and its decomposition is kinetically related to reaction rate, pore diffusion, bulk or stream diffusion and the presence of adventitious impurities (Bryers 1996). Excluded pyrite will decompose to FeS, FeO, and Fe₂(SO₄)₃ at 475 °C. When the temperature exceeds 525 °C, these minerals are not stable and will release S or SO₂, leading to the presence of liquid Fe₂O₃ at temperatures higher than 1600 °C (Bryers 1996). Included pyrites are believed to generate iron fume, and are responsible for the fluxing of silicates (Bryers 1996).

**2.3.2 Transformation of organically-bound elements**

The organically-bound elements including sodium, calcium, magnesium, and potassium are commonly found in low rank coal and biomass (Bryers 1996; Easterly et al. 1996; Tillman 2000). The fates of the organically-bound sodium and calcium are reviewed and their roles to ash deposition are discussed.
Organically-bound sodium
During combustion, the organically-bonded sodium (and NaCl) is often evaporated at early stages of burnout as the volatiles are released. Once released, NaOH is the primary gas species and can react with silicates and sulphate to form Na$_2$SiO$_3$ and Na$_2$SO$_4$, (Bryers 1996). Sodium silicates are believed to be responsible for both fouling and slagging during combustion, while the low-melting point sodium sulphate is mainly found on the heat transfer surfaces in convective areas as an initiator for fouling (Hurley et al. 1992; Hurley et al. 1993; Bryers 1996).

Organically-bound calcium
Organically-bound calcium is known to form reactive submicron CaO fume and calcium silicate cenospheres (Bryers 1996). The fume can initiate ash deposition by forming calcium-sulphate-bonded deposits on furnace walls and low-temperature convective surfaces (Bryers 1996). Meanwhile, organically-bound calcium can react with aluminosilicate and quartz to form low-temperature eutectics, leading to severe slagging problems.

2.3.3 Mineral interactions and ash formation
During combustion at high temperatures, complex physical changes and mineral interactions would also occur in addition to the mineral transformation as mentioned above. Many researchers have investigated the ash formation process among which the fates of the minerals and mineral matter are discussed (Charon et al. 1990; Hurley et al. 1992; Hurley et al. 1993; Ten Brink et al. 1995; ten Brink et al. 1996; ten Brink et al. 1997; Wigley et al. 1997; Wigley et al. 1998; Yan et al. 2001; Tomeczek et al. 2002; Zhang et al. 2006; Yu et al. 2007; Wang et al. 2008; Bai et al. 2009; Van Dyk et al. 2009; Wang et al. 2009). In general, the mineral transformation and ash formation process can be illustrated in Figure 2-3 (Tomeczek et al. 2002). It is obvious that the excluded minerals will experience transformation or decomposition, fusion, and solidification during combustion, while the minerals or organically-bound elements undergo decomposition, fragmentation, vaporization and condensation (Hurley et al. 1992).

In addition, the interactions between minerals and mineral matter would also occur in different stages of ash formation (Tomeczek et al. 2002). As a result, the ash particle
formed is heterogeneous both in ash particle size and ash chemistry (Hurley et al. 1992; Wee et al. 2006).

In summary, the transformation of mineral and mineral matter during combustion is dependent on the coal type, temperature, atmosphere, and other conditions, leading to different mineral phases in the ash. In addition, the sizes of these types of minerals vary significantly during combustion, leading to wide size distribution of the ash particles. Therefore, understanding the mineral transformations and interactions are quite essential to comprehend ash properties and their roles during ash deposition.

![Diagram of mineral transformation and ash formation process during coal combustion](Reproduced from Tomeczek et al. 2002)

**2.4. Ash characterisation**

The review on the mineral matter in coal and their transformations during combustion has provided a basis to understand the existing forms of these inorganic species during combustion. However, ash deposition is a physicochemical process that, not only are the transformation and interaction of mineral matter relevant, the physical changes such as particle softening and ash fusion are also vital in this process. Therefore, further properties of the ash are required to characterise and evaluate the ash behaviour during combustion. To achieve these, the ash viscosity, ash fusibility, and ash sintering characteristics are discussed in this section.

**2.4.1 Ash Viscosity**

Viscosity is the primary physical property to assess the flow, sintering, and slagging properties of coal ash (Raask 1985; Al-Otoom et al. 2000). It is also a dominant factor
that governs the initial ash deposition (Srinivasachar et al. 1991) and the strength development of the deposit (Raask 1985; Bryers 1996). The ash viscosity can be measured by various methods based on the assumption that the liquid slag behaves as newton liquid (Bryers 1996) or non-newton liquid (Tonmukayakul et al. 2002).

Ash viscosity is related to the chemistry and mineralogy of the ash as well as the temperature and atmosphere the ash subjecting to. Fluxing minerals such as sulphate, silicate, anhydrite, plagioclases, K feldspars, Ca silicates and hematite lead to low viscosity and high flow characteristics of ashes and slags (Vassilev et al. 1995). Alkaline or alkaline earth oxides contents in ash tend to decrease the viscosity of aluminosilicate with the exception that potassium increase the viscosity in aluminosilicate slags (Raask 1985). Iron oxides also play an important role in determining the viscosity of coal ashes. Detailed review on the role of iron oxides can be found in previous section. In addition, the viscosity of an ash is also dependent on the atmosphere the ash subjecting to. In reducing atmospheres in which more fluxing minerals are formed, the viscosity of an ash will be decreased. In particular, FeO is a strong fluxing agent in reducing atmosphere, which can be separated into liquid metal, and alloyed with silicon. However, in oxidising atmosphere, the ferric iron will not flux the melt, and the crystallisation of iron spinels and iron-containing silicates will lead to an increase in viscosity (Raask 1985; Bool Iii et al. 1995).

2.4.2 Ash Fusibility

Ash fusibility is a basic characteristic to assess the propensity of ash to ash slagging and fouling during combustion at high temperatures. The conventional method for ash fusibility characterisation in Australia is described in (Wall et al. 1999). This method measures the dimensional changes of an ash cone as a function of temperature during which four characteristic temperatures including deformation temperature (DT), softening temperature (ST), hemisphere temperature (HT), and flow temperature (FT) are identified. If the ash fusion temperatures are low, ash particle will be easily fused and become adhesive during combustion, and then integrate into large particles or adhere onto the heat transfer surfaces. In reality, ash fusion temperatures (AFT) have been applied to instruct the utilisation of coal and coal blends (Jak 2002). DT is often used as a basis for selection of furnace exit gas temperature. In addition to ash fusion test, improved ash fusion test (Wall et al. 1998; Kahraman et al. 1999; Reifenstein et al. 1999), and Thermo-mechanical analysis (TMA) (Gupta et al. 1998; Wall et al. 1998;
Wall et al. (1999) are also used to determine the ash fusion temperatures. Empirical indices and thermodynamic equilibrium calculations have also been used to predict ash fusion temperatures. Typical indices include the Basic/Acid ratio, Silica/Alumina ratio and iron content in coal (Raask 1985; Jak et al. 1998; Yan et al. 2001; Jak 2002).

During ash fusion process, complex physicochemical changes such as sintering, melting, mineral transformation and interaction would occur (Wall et al. 1998; Jak 2002). The correlation of ash fusibility with mineral and chemical composition has been investigated by various researchers. Vassilev et al. (Vassilev et al. 1995) investigated the influence of mineral and chemical composition of coal ashes on their fusibility. They found that lower AFT is related to increased proportions of the fluxing sulphate, silicate and oxide minerals such as anhydrite, acid plagioclases, K feldspars, Ca silicates, and hematite in high temperature coal ashes, while higher AFT is a result of decreased concentrations of the fluxing minerals and increased concentrations of the refractory minerals such as quartz, metakaolinite, mullite, and rutile in these ashes. Moreover, the low-melting point eutectics as shown in Table 2-1 are also responsible for low fusion temperatures of certain ashes. In addition, AFT are dependent on gas atmosphere. Ash fusion temperatures in reducing atmosphere are commonly lower than those in oxidizing temperatures (Raask 1985; Jing et al. 2013).

However, the application and accuracy of the ash fusion test have been questioned along with its birth as it is more like a qualitative observation (Gupta et al. 1998; Wall et al. 1998; Kahraman et al. 1999; Wall et al. 1999; Goñi et al. 2003). In addition, the initial deformation temperature that determined during ash fusion test is confirmed not to be the initial temperature that the ash becomes soft as significant amount of liquid phase has been formed at DT (Al-Otoom et al. 1999). Instead, the actual onset temperature for ash become soft is the sintering temperature, a temperature that is far lower than DT as determined.

2.4.3 Ash Sintering
Sintering refers to the bonding or welding of adjacent particles in a powder medium under the influence of excess surface energy (Al-Otoom et al. 2000). It is a major contributor to a number of ash-related problems such as ash deposition, and bed agglomeration (Skrifvars et al. 1992; Al-Otoom et al. 2000). This phenomena occurs at
temperatures well below the onset of melting-the initial deformation temperature by standard ASTM (Bryers 1996).

Table 2-1: A summary of low temperature eutectics during ash fusion process

<table>
<thead>
<tr>
<th>Author</th>
<th>Eutectics or minerals</th>
<th>Eutectic temperature or melt temperature (°C)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall, T.F., et al</td>
<td>SiO₂·Al₂O₃·K₂O</td>
<td>923</td>
<td>K-rich</td>
</tr>
<tr>
<td>(Wall et al. 1998)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall, T.F., et al</td>
<td>SiO₂·Al₂O₃·K₂O</td>
<td>985</td>
<td>K-poor</td>
</tr>
<tr>
<td>(Wall et al. 1998)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall, T.F., et al</td>
<td>SiO₂·FeO·CaO</td>
<td>1093</td>
<td></td>
</tr>
<tr>
<td>(Wall et al. 1998)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall, T.F., et al</td>
<td>SiO₂·Al₂O₃·FeO</td>
<td>1088</td>
<td>Start of iron</td>
</tr>
<tr>
<td>(Wall et al. 1998)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall, T.F., et al</td>
<td>SiO₂·Al₂O₃·FeO</td>
<td>1205</td>
<td>Iron join with mullite</td>
</tr>
<tr>
<td>(Wall et al. 1998)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wall, T.F., et al</td>
<td>SiO₂·Al₂O₃·CaO</td>
<td>1310, 1315, 1335, 1345</td>
<td></td>
</tr>
<tr>
<td>(Wall et al. 1998)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bryers (Bryers 1996)</td>
<td>Na₂S₂O₇</td>
<td>404</td>
<td>SO₃ level &gt; 200ppm</td>
</tr>
<tr>
<td></td>
<td>K₂S₂O₇</td>
<td>393</td>
<td>SO₃ level &gt; 2000ppm</td>
</tr>
</tbody>
</table>

The ash sintering temperature may be determined using different methods based on the changes in thermal conductivity, strength and viscosity of the ash as well as the changes of its physical dimensions (Al-Otoom et al. 1999; Al-Otoom et al. 2000). Various experimental techniques, such as thermal conductivity analysis (TCA), thermo-mechanical analysis (TMA), heating microscopy, compression strength (CS) and pressure-drop technique have been reported in the literature (Al-Otoom et al. 1999; Al-Otoom et al. 2000; Li et al. 2016). Among the various experimental techniques, the pressure-drop technique stands out due to many advantages such as its simplicity, high sensitivity to dimension changes and ability to simulate real atmosphere, and high accuracy (Li et al. 2016).

The dominant mechanism during sintering is the viscous flow (Raask 1985). During sintering, complex physical-chemical changes including the reduction in porosity, the
changes in shrinkage and deposit strength, the eutectic formation and the interaction between mineral phases would occur (Al-Otoom et al. 2000).

Sintering is also accompanied by the mineral transformation and interactions, and the eutectics formation (Skrifvars et al. 1992; Nowok et al. 1998; Al-Otoom et al. 1999; Al-Otoom et al. 2000; Abd-Elhady et al. 2007; Haykiri-Acma et al. 2010; Jing et al. 2011). The fluxing minerals will decrease sintering temperature while the refractory minerals will increase sintering temperature (Vassilev et al. 1995). In addition, the low temperature eutectics as shown in Table 2-2 are also responsible for sintering. In particular, Fe$^{2+}$ would react with other ash constituents to form liquid phases at temperatures as low as 700 °C (Song et al. 2009; Van Dyk et al. 2009; Jing et al. 2011). The sodium–calcium silicate can react with SiO$_2$ to form low temperature fluxing minerals at temperatures as low as 725 °C (Jing et al. 2011).

Table 2-2 A summary of low temperature eutectics during sintering process

<table>
<thead>
<tr>
<th>Author</th>
<th>System or minerals</th>
<th>Eutectic or fusion temperature (°C)</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Song, W.J., et al (Song et al. 2009), Van Dyk, J.C., et al (Van Dyk et al. 2009)</td>
<td>Some Fe$^{2+}$ will be converted to Fe$^{3+}$, and Fe$^{2+}$ will react with other ash constituents</td>
<td>700</td>
<td>Reducing atmosphere</td>
</tr>
<tr>
<td>Jing, N., et al. (Jing et al. 2011)</td>
<td>Na$_2$O$_2$SiO$_3$ + SiO$_2$ + Na$_2$O$_3$CaO$_6$SiO$_2$</td>
<td>725</td>
<td>FACT-sage calculations</td>
</tr>
<tr>
<td></td>
<td>Na$_2$O$_2$SiO$_3$ + Na$_2$O$_3$SiO$_2$ + 2Na$_2$O$_3$CaO$_3$SiO$_2$</td>
<td>821</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na$_2$O$_2$SiO$_3$ + SiO$_2$</td>
<td>790</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na$_2$O$_2$SiO$_3$ + Na$_2$O$_2$SiO$_3$</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO$_2$FeO + SiO$_2$ + CaSiO$_3$</td>
<td>1095</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2FeO$_2$SiO$_3$ + SiO$_2$</td>
<td>1180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO$_2$Al$_2$O$_3$ + 2SiO$_2$ + a-CaO$_2$SiO$_3$</td>
<td>1299</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO$_2$Al$_2$O$_3$ + 2SiO$_2$ + a-CaO$_2$SiO$_3$</td>
<td>1265</td>
<td></td>
</tr>
<tr>
<td>Steck, L.V. et al (Steck et al. 1929)</td>
<td>Na$_2$S-FeS</td>
<td>640</td>
<td>$H_2$ atmosphere</td>
</tr>
</tbody>
</table>

18
In addition, sintering temperature is also influenced by gas atmosphere and pressure (Nowok et al. 1998; Haykiri-Acma et al. 2010; Jing et al. 2011). High pressure decreases the sintering temperature by facilitating the interaction of minerals and accelerating, and the reducing atmosphere often promoted eutectics formation, decreasing the sintering temperature of the ash (Jing et al. 2011).

In summary, the viscosity, fusion temperatures and sintering temperature of the ash and their relations to the ash chemistry and mineralogy, temperature, and atmosphere discussed in this section provide more details for understanding of ash properties, and evaluation of the ash behaviour during combustion. Viscosity of the ash is the fundamental property to assess sintering, fusion, and deposition behaviours of an ash. Ash fusion temperatures provide a means to evaluate the propensity of ash to softening and slagging. However, DT is not the initial temperature that the ash particles become soft. Instead, sintering temperature determines the onset temperature that the particles become soft, and provides an accurate mean to evaluate the fouling propensity of ash.

Nonetheless, cautions need to be taken in preparing ash samples. Firstly, for the same coal, the ash properties are dependent on ashing temperature. The low temperature ashes often have low sintering and fusion temperatures, while the high temperature ash has higher sintering and fusion temperatures due to their difference in ash chemistry and mineralogy (Jing et al. 2013; Jing et al. 2013). Secondly, the properties that characterised, identified and measured are the overall performance of the “bulk” ash, which is slightly different from the ash deposits following ash deposition process. Ash deposition is a selective deposition process that not all ash samples are deposited as the deposit grow (Baxter 2000). This means that the ash chemistries and structures of the ash deposit maybe varied across the deposit thickness. Therefore, the viscosity, fusion temperatures and sintering temperature of the ash are capable of but limited of evaluating the propensity of the ash to sintering and slagging. More details in ash deposition mechanism and deposits characteristics are required.

2.5 Ash deposition
This section reviews the mechanisms of ash deposition, how deposits grow and deposit strengthen develops, the deposit characteristics, and the current prediction/modelling of ash deposition.
2.5.1 Deposition mechanisms

Ash deposition mechanisms have been investigated by many researchers and have been summarised by Raask (Raask 1985), Baxter (Baxter 2000), and Dongke (Zhang 2013) etc.. Overall, a suite of ash deposition mechanisms including condensation of gas vapours, thermophoresis of fine ash particles, inertial impaction and sticking of coarse ash particles, and chemical reactions are at play:

**Condensation**

Condensation is the deposition mechanism by which vapours are deposited on surfaces cooler than the local gas (Baxter 2000). It can be divided into heterogeneous condensation and heterogeneous condensation considering the ways the vapours are deposited (Raask 1985). The condensed deposits consist of particles less than 0.5 µm and are more uniformly deposited on the tube. In pulverised coal-fired utility boilers where the fume temperature is very high, the condensates often include alkali and alkali earth species and some fine SiO\textsubscript{2} fume. These condensates are tacky, and to large degree, are responsible for the initiation of ash deposition particularly for ash fouling. Condensation is strongly temperature dependent and leads to spatial variation in ash deposit composition.

**Thermophoresis**

Thermophoresis is a deposition process of particles in a gas due to the local temperature gradient between the gas and the heat transfer surfaces (Raask 1985). It is a dominant mechanism for the deposition of fine particles with sizes less than 10 µm. The deposit is evenly distributed around the tube surface and responsible for initial stages of deposit formation.

The driving force for the thermophoresis deposition is the thermophoresis force,

\[ F_T = -6\pi\mu_d d_p f(Kn)\nabla T_g \]

where \( f(Kn) \) depends on particle diameter, Knudsen number, and several material-specific properties. Temperature gradient is crucial for thermophoresis deposition. In the hot zones of a boiler where the temperature gradient between gas and the heat transfer surface is high, thermophoresis deposition is significant (Raask 1985; Baxter 2000). However, as the thickness of the deposit layer or the temperature of the heat transfer surface increases, the effect of thermophoresis deposition decreases due to the decrease in temperature gradient.
**Inertial impaction and particle sticking**

Inertial impaction is the transportation of ash particles which have sufficient inertia to traverse the gas stream lines and deposit on heat transfer surfaces. It is a dominant deposition process for the bulk ash deposit. This process is most important for particles with sizes larger than 10 µm, resulting in the formation of a coarse-grained deposit.

The driving force of inertial impaction is a function of the particle’s Stokes Number, which is defined for a cylinder in cross flow as

\[ St = \frac{\rho_p d_p^3 \langle u_p \rangle}{9 \mu_g d_c} \psi \]

where \( \rho_p \), \( d_p \), and \( \langle u_p \rangle \) represent particle density, diameter, and mean velocity, respectively, and \( \mu_g \) and \( d_c \) represent gas viscosity and tube diameter. \( \psi \) is a correction factor that is only important when the particles do not obey Stokes’ law, i.e., large particles with high velocities relative to the gas.

However, it is worth noting that not all the impacted ash particles will stay on the surfaces or the deposit surfaces. Figure 2-4 illustrates the potential pathways of the ash particles after they impact on a heat transfer surface (Troiano et al. 2014). It is obvious that the ash particles are able to leave the surface once impacted through rebounding or splashing, a typical selective deposition mechanism that differs from condensation or thermophoresis mechanism.

![Figure 2-4](image) Interactions between the ash particles and the heat transfer surface: regimes (a) SW–SP; (b) SW–NSP; (c) NSW–SP; and (d) NSW–NSP. (1) Pre-impact, (2) impact, and (3–6) post-impact (Reproduced from Troiano et al. 2014)
Chemical reactions
Chemical reactions are the fourth of the principal mechanisms by which mass can be accumulated in a deposit (Baxter 2000). These reactions involve the reaction of the gas with the components in the deposit, or with the deposition surface itself including sulphation of alkali and alkali earth contents, alkali absorption, oxidation reactions. Chemical reactions are strongly temperature dependent, leading to spatial variation in ash deposit composition.

2.5.2 Deposition growth and strength development
The deposition mechanisms describe how ash particles are transported to the heat transfer surfaces. However, ash deposition is a dynamic process and the deposits are progressively developed. The rate of ash deposition at typical residence time is described as (Baxter 2000):

\[
\frac{dm_i}{dt} = I_i(\tau,t)G_i(\tau,t) + E_i(\tau) + T_i(\tau,t) + C_i(\tau,t) + R_i(\tau,t)
\]

where \(m_i\) represents the mass of component i in the deposit. The factor \(I_i\) represents the rate of inertial impaction, \(G_i\) the particle capture efficiency, \(E_i\) the eddy impaction rate, \(T_i\) the rate of thermophoretic deposition, \(C_i\) the rate of condensation, and \(R_i\) the rate of chemical reaction. The subscript i refers to each of the inorganic components in the raw coal. During ash deposition process, the rate of ash deposition varies and different ash deposition mechanism also has its own significance during ash deposition at different stages.

Initial stage of ash deposition
The heat transfer surfaces are initially clean, pure, and non-sticky. Once the non-sticky coarse ash particles impact on the heat transfer surfaces, these particles will bounce back and leave the surfaces as shown in Figure 2-4. However, the sticky coarse ash particles have the chance to stick onto the heat transfer surfaces. Most importantly, the gas vapours and fine particles were able to deposit on the heat transfer surfaces through condensation and thermophoresis deposition. As a result, the initial stage of ash deposition consists of condensed species, fine particles and occasionally, the sticky coarse ash particles.
Subsequent stages of ash deposition

Once the ash deposition is initiated and an inner deposition layer is formed, the non-sticky coarse particles have more chance to stay on the deposit surface after impaction. Even though the condensation of gas vapours and the thermophoresis deposition are still at play, inertial impaction of coarse ash particles begins to dominate the subsequent deposition stage.

As deposition proceeds, the characteristics of ash deposition and the behaviours of ash deposits such as deposit thickness, deposition rate, thermal conductivity, deposit structure, deposit strength and removability are also varied (Srinivasachar et al. 1991; Senior 1997; Hurley et al. 1998; Michelsen et al. 1998; Naruse et al. 2005; Rushdi et al. 2005). The strength of the deposit develops as the deposit grows. The deposit on heat transfer surface increase the heat transfer resistance between the gas and the steam. As the deposit develops, the temperature of the deposit surface also increases due to the increase in heat transfer resistance. As a result, the strength of the deposit increases, progressively leading to sintered, semi-fused, and even fused ash deposit. Depending on the fire side temperatures, ash deposition is further categorized into slagging and fouling. Slagging is the ash deposition in the radiative heat transfer sections of the boiler, whereas fouling is the ash deposition in the convective heat transfer sections (Wall et al. 1993; Bryers 1996).

Slagging

Slagging can cause three operation problems during combustion (Su et al. 2001): firstly, slag can build up on the wall, which increase the thermal resistance of heat transfer surface; secondly, slag can increase corrosion; and thirdly, slag can drop and/or fall into the bottom of the furnace, which can damage the tubes and block the hoppers.

In general, without ash removal mechanisms such as soot blowing, the formed ash slag has three layers (Erickson et al. 1995; Gupta et al. 2002). An initial layer is adjacent to the wall, which is often formed by fine ash particles, resulting in the formation of particulate deposit. A middle layer is the bulk layer of the deposit formed by deformable and non-deformable ash particles, which is often partially melted or sintered. An outer layer of the deposit is at the deposit outer surface, which is often fused.
The formation of slags is a complex physical-chemical process (Bryers 1996). Initially, the fine ash particles or sticky particles would arrive at the surfaces of tube, leading to the irregular surface and increasing temperature of the ash particles (Raask 1985; Erickson et al. 1995). As temperature increases, particles with low melting temperature begin to sinter, deform, and eventually melt, leading to the presence of liquid phases (Bryers 1996). The presence of liquid phases increases the capture of sticky and non-sticky ash particles, leading to rapid growth of the ash deposit and an increase in the size of the deposit (Wee et al. 2006). These deposits can react with other components in the forms of gas phases, solid phases and liquid phases, leading to increased melting and mineral interactions (Benson 1998). As a result, ash slags are formed with the deposit surface completely melted. Under the influence of gravity, deposit shedding sometimes can occur, leading to repeated and shedding of ash deposits (Su et al. 2001; Sato et al. 2015).

Depending on the types of coal, the chemistry of the deposit layers is also different. For high rank coals, the initial layers of ash slag are enriched with potassium-bearing silicates, free quartz, and submicron iron. Subsequent layers develop like drop-wise condensation, which build from random sites on the tube surface. The outer layer of the ash slag, which mainly consists of fused slag, is composed of rapidly quenched, subcooled glassy silicates (Bryers 1996). Low rank coals have an increased proportion of organically-bound mineral matter such as sodium, and calcium, thus the slagging process is different from high rank coals (Bryers 1996). For low rank coals, the initial layer of the ash slag consists of submicron particles including calcite, calcium sulphate, and clays due to the increased proportion of inherent mineral matter and organically-bound calcium. The subsequent layers, which mainly consist of eutectic mixtures of anorthite, gehlenite and pseudo-wollastonite, can easily reach equilibrium and simply melt due to their low melting temperatures. The outer layer of fused slags is thus thinner and has higher surface temperatures (Bryers 1996).

**Fouling**

Fouling refers to ash deposition in convective heat transfer areas. Fouling deposits also decrease heat transfer coefficients, increase corrosion and have the potential to fall or drop as the deposit accumulates.
Compared to slagging deposits, fouling deposits usually do not contain high levels of liquid phases (Su et al. 2003). However, the deposit characteristics vary dramatically from strong, highly molten deposits to weak, powdery deposits (Erickson et al. 1995). The structure of ash deposits of fouling generally consists of an inner layer which mainly consists of fine particulate and condensed vapours primarily alkali and alkaline earth sulphates, the middle layer of partially fused or molten ash or lightly sintered particles usually enriched in basic constituents, and the outer layer with semi-fused or sintered ash that has a composition similar to the entrained fly ash (Couch 1994; Erickson et al. 1995; Su et al. 2003; Kalisz et al. 2005).

It is worth noting that fouling is frequently caused by the condensation and chemical reaction of volatile alkali and alkali earth mineral matter with fly ash either in the gas stream or at the tube surface, initiating ash deposition and making the surface receptive to collect other species normally found to be innocuous (Bryers 1996). The most common deposits includes alkali-bonded deposits and calcium-sulphate-bonded deposits (Bryers 1996). The propensity of ash fouling is dependent on coal rank. High rank coal often has less content of alkali and alkali earth, and therefore less fouling problems. Low rank coal such as lignite, however, has higher contents of fluxing alkali and alkali earth contents, and therefore severe ash fouling problem.

2.5.3 Approaches for evaluation of ash deposition

The propensity of ash slagging and fouling have been extensively studied in literature (Couch 1994; Bool Iii et al. 1995; Erickson et al. 1995; Ram et al. 1995; ten Brink et al. 1996; Bryant et al. 1998; Heinzel et al. 1998; Jak et al. 1998; McLennan et al. 2000; Rezaei et al. 2000; Kondratiev et al. 2001; Su et al. 2001; Russell et al. 2002; Rushdi et al. 2005; Barroso et al. 2006; Kupka et al. 2008; Degereji et al. 2012), and are summarised in Table 2-3 and Table 2-4, respectively. There are different approaches to evaluate or predict ash fouling and slagging propensities including indices, thermal equilibrium calculation, and experimental approaches. However, the indices are empirical and sometimes fail to predict the propensities of slagging and fouling. Moreover, empirical indices based on bulk ash chemistry and viscosity fail to consider the heterogeneity of ash deposit and empirical indices based on heat transfer and build-up rate sometimes will get misleading results due to deposit shedding. Thus, more efforts should be done in assessing the propensities of ash slagging and fouling.
Thermodynamic equilibrium calculations are also used to predict slagging and fouling propensity by the calculation of liquid and solid phases at equilibrium state. Modelling of slagging propensities need to consider the ash removability, growth rate, and heat transfer (Erickson et al. 1995; Senior 1997). With the advance techniques such as CCSEM, QemSCAN, and other micro-analytical techniques, the size distribution of minerals of excluded and included, mode of occurrence of elements and other details can be obtained as input of these modelling, and would able to provide more accurate modelling.

In summary, ash deposition process is a complex, selective, and dynamic process that relates to mineral matter in coal, operating conditions and boiler design. The variations in time, temperature and spaces also lead to differences in ash deposition process, ash mineralogy and chemistry, and therefore deposit behaviours. The above review provides a sound basis to understand ash deposition and deposit behaviour. However, investigations are needed to not only understand the ash deposition problem, but also a step further to manage and mitigate ash deposition during combustion as reviewed in the next section.
Table 2-3 Literature methods and approaches for the evaluation of the ash slagging propensities

<table>
<thead>
<tr>
<th>Author</th>
<th>Basis</th>
<th>application</th>
<th>Slagging index</th>
<th>Slagging propensity</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raask (Raask 1985)</td>
<td>Ash fusion temperatures</td>
<td>All fuels</td>
<td>(4IDT+HT)/5</td>
<td>&gt;1343 °C: 1232-1343 °C: 1149-1232 °C: &lt;1149 °C</td>
<td></td>
</tr>
<tr>
<td>Corrosion, A.R.C.O, et al (Corrosion et al. 1974)</td>
<td>Viscosity</td>
<td>All fuels</td>
<td>Temperature at which viscosity changes from Bingham Plastic to Newtonian T_v ≈ T_{soften}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion, A.R.C.O, et al (Corrosion et al. 1974)</td>
<td>Viscosity</td>
<td>All fuels</td>
<td>R_v = (T_{250(ox)}-T_{10000(re)})/975 Fs</td>
<td>&lt;0.5: 0.5-0.99: 1.0-1.99: &gt;2.0</td>
<td></td>
</tr>
<tr>
<td>Corrosion, A.R.C.O, et al (Corrosion et al. 1974)</td>
<td>Viscosity</td>
<td>All fuels</td>
<td>temperature at 250 poise-the critical limit for slag tapping</td>
<td>&gt;2325T (dry bottom): 2250-2100T (dry bottom): 2275-2500T (dry bottom): &lt;2200T (dry bottom)</td>
<td>0.5 max for dry bottom &gt;0.27 min. for wet bottom</td>
</tr>
<tr>
<td>Raask (Raask 1985)</td>
<td>Viscosity</td>
<td>All fuels</td>
<td>Log(u)=m×10^{7}/(T-150)^{2}+C</td>
<td>High viscosity yields low slagging potential</td>
<td></td>
</tr>
</tbody>
</table>
## Chapter 2 Literature Review

<table>
<thead>
<tr>
<th>Author</th>
<th>Basis</th>
<th>Application</th>
<th>Slagging index</th>
<th>Slagging propensity</th>
<th>Evaluations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion, A.R.C.o, et al (Corrosion et al. 1974)</td>
<td>Ash chemistry</td>
<td>All fuels</td>
<td>B/A ratio = ([Fe₂O₃+CaO+MgO+K₂O+Na₂O]/(SiO₂+Al₂O₃+TiO₂))</td>
<td>Low Medium high Severe</td>
<td>Eutectics formed between 0.3 and 3.0 increase slagging; Slagging is the worst when the ratio is around 1.0 (Su et al. 2001);</td>
</tr>
<tr>
<td>Corrosion, A.R.C.o, et al (Corrosion et al. 1974)</td>
<td>Ash chemistry</td>
<td>eastern bituminous</td>
<td>Rs=(B/A) (%S on dry coal)</td>
<td>&lt;0.6 0.6-2.0 2.0-2.6 2.6</td>
<td></td>
</tr>
<tr>
<td>Russell, N.V, et al (Russell et al. 2002)</td>
<td>EFR slagging index</td>
<td>All fuels</td>
<td>B/A ratio × Fe₂O₃ % of points falling within the defined CaO and or Fe₂O₃ limits Cao limits: 5-40wt%; Fe₂O₃ limits: 10-50 wt%</td>
<td>Considered excluded and included iron-bearing minerals</td>
<td></td>
</tr>
<tr>
<td>McLennan, A.R., et al. (McLennan et al. 2000)</td>
<td>Ash chemistry</td>
<td>Iron-rich coals</td>
<td>X(T)OX = ([Fe₂O₃+FeS₂+FeS]excl<em>E(T)OX + (1-R)</em>[Fe₂O₃+FeS₂+FeS]incl<em>E(T)OX + R</em>[Fe₂O₃+FeS₂+FeS+SiO₂+SiO₂-Al₂O₃]incl*D(T)OX] *kg ash/tonne coal</td>
<td>Intensive slagging occurs in range of 0.75-2; others decrease the slagging intensity</td>
<td></td>
</tr>
<tr>
<td>Heinzel, T., et al. (Heinzel et al. 1998)</td>
<td>Ash chemistry</td>
<td>Co-fire with biomass</td>
<td>Sl=fluxing oxides /sintering oxides=[Fe₂O₃+CaO+MgO+K₂O+Na₂O+P₂O₅]/(SiO₂+Al₂O₃+TiO₂)</td>
<td>The higher build-up rate, the higher slagging propensity Deposit shedding sometime occurs</td>
<td></td>
</tr>
<tr>
<td>Su, S., et al (Su et al. 2001)</td>
<td>Build-up rate</td>
<td>All fuels</td>
<td>Ash deposition thickness after a period</td>
<td>The higher heat flux ratio, the less slagging propensity Deposition shedding sometime occurs</td>
<td></td>
</tr>
<tr>
<td>Su, S., et al (Su et al. 2001)</td>
<td>Heat flux</td>
<td>All fuel</td>
<td>The minimum heat flux ratio and total heat flux ratio</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Chapter 2 Literature Review

<table>
<thead>
<tr>
<th>Author</th>
<th>Basis</th>
<th>application</th>
<th>Slagging index</th>
<th>Slagging propensity</th>
<th>Evalations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barroso, J., et al.</td>
<td>Build up rate</td>
<td>capture efficiency (CE) and</td>
<td>Low, Medium, high, Severe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Barroso et al. 2006)</td>
<td></td>
<td>energy-based growth rate (GRE)</td>
<td></td>
<td></td>
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<tr>
<td>Degereji, M.U., et al.</td>
<td>Viscosity</td>
<td>All fuels</td>
<td>$S_x = r \log(u)$; $r$ - the weight of ash in coal, $u$ - ash viscosity</td>
<td>Low, Medium, high,</td>
<td>Successfully predict</td>
</tr>
<tr>
<td>(Degereji et al. 2012)</td>
<td></td>
<td></td>
<td></td>
<td>high, Severe</td>
<td>slagging performance of 4</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>blends</td>
</tr>
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</table>
### Table 2-4  Methods and approaches in the literature for the evaluation of the ash fouling propensities

<table>
<thead>
<tr>
<th>Author</th>
<th>Basis</th>
<th>application</th>
<th>fouling index</th>
<th>Fouling propensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion, A.R.C.o.et al (Corrosion et al. 1974)</td>
<td>Alkali content of coal</td>
<td>All fuels</td>
<td>%Na₂O in the ash</td>
<td>Low: &lt;2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Σ(%Na₂O +0.6589 %K₂O)</td>
<td>Medium: 2-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Lignite bituminous</td>
<td>High: 6-8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>&gt;8</td>
<td>severe: &gt;8</td>
</tr>
<tr>
<td>Corrosion, A.R.C.o.et al (Corrosion et al. 1974)</td>
<td>Alkali content of coal</td>
<td>eastern bituminous coal</td>
<td>Σ(%Na₂O +0.6589 %K₂O) (%ash/100)</td>
<td>Low: &lt;0.3</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Medium: 0.3-0.45</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High: 0.45-0.6</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>severe: &gt;0.6</td>
</tr>
<tr>
<td>Corrosion, A.R.C.o.et al (Corrosion et al. 1974)</td>
<td>Ash sintering strength</td>
<td>All coals</td>
<td>Compression strength</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000-5000</td>
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<td></td>
<td>5000-16000</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;16000</td>
</tr>
<tr>
<td>Corrosion, A.R.C.o.et al (Corrosion et al. 1974)</td>
<td>Chlorine</td>
<td>All coals</td>
<td>% Cl in coal</td>
<td>Low: &lt;0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Medium: 0.2-0.3</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High: 0.3-0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>severe: &gt;0.5</td>
</tr>
<tr>
<td>Corrosion, A.R.C.o.et al (Corrosion et al. 1974)</td>
<td>Ash chemistry</td>
<td>eastern bituminous only</td>
<td>Rₛ=(B/A)[%Na₂O (ASTM ash)]</td>
<td>Low: &lt;0.2</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Medium: 0.2-0.5</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>High: 0.5-1.0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>severe: &gt;1.0</td>
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<tr>
<td>Su, S., et al (Su et al. 2003)</td>
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<td></td>
<td></td>
<td></td>
<td>Heat transfer coefficient</td>
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<td></td>
<td></td>
<td></td>
<td>U=Cₚm(Tₐ-Tₜ)/S(Tₐ-Tt)</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Low U indicates high fouling propensity</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Build-up rate</td>
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<td>Build-up rate g/h</td>
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<td></td>
<td></td>
<td>High build-up rate indicates high fouling propensity</td>
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<td></td>
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<td></td>
<td>Deposit growth rate (mm/h)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>High deposit growth rate indicates high fouling propensity</td>
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<td></td>
<td>FGET/IDT(ox)</td>
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<td></td>
<td>FGET- flue gas exit temperature</td>
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<td></td>
<td></td>
<td></td>
<td>A linear correlation with Na₂O g/GJ</td>
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<td></td>
<td></td>
<td></td>
<td>Quantity of alkali per unit of fuel energy (1/Q)Yash(YK₂O+ YNa₂O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ash chemistry</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Quantity of Na₂O per unit of fuel energy, g/GJ</td>
<td></td>
</tr>
</tbody>
</table>
2.6 Ash deposition mitigation strategies

As mentioned above, ash deposition is related to the mineral matter in coal, the operating conditions and the boiler design. On a larger scale, understanding the ash deposition problem is to provide guidance for the boiler design, and to manage and control ash deposition to an “acceptable” degree so that the practical utility boilers are economically and efficiently operated. To achieve these, great efforts have been made in managing and mitigating ash deposition using different methods starting from changing the mineral matter in coal, and optimizing the operating conditions and the boiler design (Vuthaluru et al. 1998; Su et al. 2001; Öhman et al. 2004; Rushdi et al. 2004; Gupta 2005; Lokare et al. 2006; Takuwa et al. 2007; Tillman et al. 2007; Wigley et al. 2007; Naganuma et al. 2009; Zbogar et al. 2009; Li et al. 2010; Akiyama et al. 2011; Ctvrtnickova et al. 2011; KonSomboon et al. 2011; Duan et al. 2013; Huang et al. 2013; Näzelius et al. 2013; Wang et al. 2014; Zhou et al. 2014). These approaches include optimizing the temperature distribution of the furnace, the air distribution of the furnace, optimizing the surface properties of the heat transfer surface, and of particularly concern, changing the properties of the fuel through coal blending, adding additives, and water washing.

2.6.1. Effect of coal blending

Coal blending has been extensively used in practical power stations due to economical (fuel prices, transportation, and supply), environmental (emissions of NOx, SOx, and particulate matter), and technical benefits (ash fouling and slagging) (Raask 1985; Su et al. 2001; Rubiera et al. 2002; Su et al. 2003; Wang et al. 2008; Wang et al. 2009; Tillman et al. 2012). Many studies have been carried out to investigate the effect of coal blending on the ash properties and the ash deposition behaviour (Qiu et al. 1999; Qiu et al. 1999; Bryant et al. 2000; Rushdi et al. 2004; Liu et al. 2013; Lee et al. 2015).

In studying the ash fusion characteristics of blended coals, Qiu et al (Qiu et al. 1999; Qiu et al. 1999) reported that blended ash softening temperatures are not linearly related to the blending ratios. They found that the production of low-melting eutectics in blended ash minerals at high temperature is responsible for the non-linear relationship between blended ash-melting temperature and blending ratios. Similar conclusion was also applied in Bryant’s work (Bryant et al. 2000) when they studied the variation in fusibility of blended coal ashes with blending on the basis of varying Fe$_2$O$_3$, Si/Al ratio
and CaO content. They also found that the trends in AFTs with different blending ratio are mirrored by the changes in the liquidus temperature. Furthermore, they proposed the use of TMA to characterise the ash fusibility, a better means to evaluate ash fusibility than the conventional ash fusibility test.

When studying the effect of coal blending on ash deposition, Rushdi et al (Rushdi et al. 2004; Rushdi et al. 2005) found that blends behaviour was not additive in nature due to the interactions between ash particles within the deposit layer. They concluded that the coal blending leads to different ash deposition behaviour compared to that of the source coals. In addition, Su et al (Su et al. 2001; Su et al. 2003) also evaluated the fouling and slagging propensities of blend coals during pulverized coal-fired boilers. They found that the slagging propensity of coals and blends varied and the worst slagging occurring when the Fe$_2$O$_3$/CaO molar ratio approaches 1.0.

These studies reveal that the effect of coal blending on ash deposition is non-linear with the blending ratio and is likely to have a significant influence on ash deposition. The mineral matter in the blended coal may be differed from the designed coal for a boiler, which would lead to serious ash fouling and slagging problems. Therefore, understanding the mineral matter in the parent coals, their transformation and interaction, the deposition mechanism and behaviour during combustion of blended coal is still valuable while managing ash deposition using coal blending.

2.6.2. Effect of additives

Addition of additives is another method to change the ash properties and manage ash deposition. This method allows the addition of aluminium silicates based additives (kaolinite, quartz, bauxite), and calcium based additives (calcite, lime, and Ca(OH)$_2$) into coal to change the mineral matter in coal, the mineral transformation and interactions, and the deposition behaviour (Vuthaluru et al. 1999; Wigley et al. 2007; Steenari et al. 2009; Akiyama et al. 2011; Konsonboon et al. 2011; Si et al. 2014; Zhang et al. 2015; Zhou et al. 2015). In mitigating ash deposition of biomass, sulphur based additives and phosphorus rich additives are also used (Wang et al. 2012).

The effect of additive addition is similar to the coal blending effect as a certain type of coal could be one source of the chosen additives. According to available results and interpretations, different mitigation mechanisms for ash deposition have been proposed,
including chemical reactions, physical adsorption, inhibiting ash melting by introducing
more refractory minerals into ash residues, and diluting the ash and restraining the
formation and accumulation of liquid phases (Wang et al. 2012).

An ideal additive should be as effective and reactive as possible in order to capture
problematic species formed during combustion and have the following properties
(Wang et al. 2012): (1) high reactivity to reduce the amount of problematic ash species
irreversibly; (2) high temperature stability; (3) large enough surface area for rapid
adsorption and high loading capacity; and (4) relative high melting point itself without
contributing to any new operating problematic issues.

The effect of additives on ash sintering behaviour and ash fusibility has been
investigated and was found to be varied with additives and ash samples (Llorente et al.
2015) investigated the effect of fine additives on the sintering behaviour of high sodium
coal ash under oxy-fuel combustion atmosphere. It was found that quartz promoted the
ash melting process but CaO greatly suppressed the sintering and melting process.
Besides, bauxite, Fe₂O₃ and kaolin to some extent affected the quantity of molten
phases. In an effort to capture the alkali species and abate the sintering behaviour of the
ash from agricultural residues, Wang et al (Wang et al. 2012) found that both kaolinite
and zeolite 24A were able to bind KCl and form potassium aluminium silicates,
however zeolite Y showed a poor ability to abate sintering of the ash. Llorente et al
(Llorente et al. 2008) investigated the effect of seven additives on the sintering of
biomass ash and found that kaolin, lime, calcined dolomite and ophite are suitable to
mitigate the biomass ash sintering in all the cases, while dolomite, limestone and the
tabular alumina offered poorer results. The dilution effect is the main reason for the
decrease of the sintering for most of the additives, with the exception of kaolin whose
chemical reactions could be more important than the dilution effect.

The effect of additives on ash deposition has also been investigated and was found that
the deposition behaviour varied with the types of coal as well as the additives
(Vuthaluru et al. 1996; Vuthaluru et al. 1998; Vuthaluru 1999; Tangsathitkulchai et al.
2001; Vuthaluru et al. 2001; Wigley et al. 2007; Akiyama et al. 2011; Huang et al.
2013; Madhiyanon et al. 2013). Wigley et al (Wigley et al. 2007) investigated the effect
of albite (NaAlSi$_3$O$_8$), calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$), orthoclase (KAlSi$_3$O$_8$), iron blast furnace (BF) slag and pulverised fuel ash (PFA) on the deposition efficiency, sintering degree and thickness of the deposits. They found that for both CTF and EFR deposits, there were significant changes in microstructure as the level of mineral addition increased: the degree of deposit sintering increased and the porosity decreased, the chemical homogeneity of the deposits increased, and a matrix with a distinct composition, richer in CaO (calcite addition) or Na$_2$O (albite addition), appeared and became abundant. These effects were strong for calcite additions, weak for albite additions, and not significant for additions of PFA. In addition, the added minerals have interacted with the coal ash in the deposition, leading to the changes in deposit microstructure and the chemistry. Vuthaluru et al (Vuthaluru et al. 1996; Vuthaluru et al. 1998; Vuthaluru 1999; Vuthaluru et al. 1999) investigated the effect of sodium-binding additives on the fouling behaviour of brown coals and found that sodium could be effectively captured by clay-type mineral additives, particularly kaolin. 2–3 wt% kaolin with particle sizes between 10–20 µm was estimated to effectively reduce fouling of the Victorian brown coal. In studying the ash deposition of biomass, Konsomboon (Madhiyanon et al. 2013) found that 8% kaolin addition is effective to capture the potassium in the fuel and mitigate the ash deposition problems. In addition, Akiyama et al (Akiyama et al. 2011) investigated the effect of MgO addition to upgraded brown coal on ash-deposition behaviour during combustion and found that MgO addition decreased the rate of ash deposition due to the production of solid-phase aluminosilicate.

These studies reveal that addition of additives is one way to manage and mitigate ash deposition. However, due to the complex mineral interactions, the careful selections of additives are crucial for one typical coal as not all the additives are able to mitigate ash deposition. In addition, the amounts of additives added to the coal are also essential so that the additives are technically-effective and economically-viable in mitigating ash deposition.

2.6.3. Effect of water washing

Water washing is also regarded as a method to mitigate or manage ash deposition, which is aimed to remove the water-soluble elements including sodium, calcium, and chlorine in the fuel prior to combustion. Therefore, water washing is mostly used in low rank coals and biomass as these fuels have abundant water-soluble inorganic elements and severe ash deposition problems (Said et al.; Benson et al. 1985; Jenkins et al. 1996;

The effect of water washing on the ash properties and ash fusibility has been investigated (Said et al.; Benson et al. 1985; Jenkins et al. 1996; Arvelakis et al. 2001; Arvelakis et al. 2002; Cheeseman et al. 2003; van Dyk et al. 2005; Skoulou et al. 2009; Li et al. 2011; Yu et al. 2014). Huang et al (Huang et al. 2013) investigated the water washing effect on the ash fusion temperatures and found that water washing would increase the mullite generation and increase the ash fusion temperatures, suggesting that water washing is effective in managing ash properties and ash deposition. However, Li et al (Li et al. 2011) investigated the water washing effect on the ash fusion temperatures of three types of lignite and found that water washing was not always effective in increasing the fusion temperatures. A decrease in AFT of HLH was observed after washing due to the increased contents of anhydrite and cordierite in the ash. In addition, Van Dyk et al (van Dyk et al. 2005) found that water washing had minor effect on the AFT of some South African coal as only minor fraction of basic elements were able to be washed out.

A few studies have also investigated the effect of water washing on the ash sintering and deposition (Vuthaluru et al. 1999; Vuthaluru et al. 1999; Arvelakis et al. 2002). Vuthaluru et al (Vuthaluru et al. 1999; Vuthaluru et al. 1999) found that water washing is an effective way to remove sodium and to mitigate bed agglomeration and de-fluidization. Meanwhile, Arvelakis (Arvelakis et al. 2002) also found that water washing was effective in removing the alkali content in the olive ash and therefore mitigate ash agglomeration.

These studies reveal that water washing seems to be one effective way to remove the water-soluble basic elements, increase the ash fusion temperatures, and to mitigate ash deposition problems. However, water washing is not always effective in mitigating ash deposition. The reason is that water washing can only remove the water-soluble species
in the coal. Moreover, in practical power stations, the large volumes of water required for the water washing of millions of tons of coal, the treatment of the resulting waste water, and the drying of washed coals need to be taken into thorough consideration.

2.7 Conclusions from Literature Review and Implications for the Current Research

Previous research has established a sound knowledge base of coal and ash characterisation, ash deposition and deposit development, deposit behaviour, and deposition mitigation strategies during pulverised coal-fired combustion. However, the current understandings of ash deposition also imply that there are areas where further research is needed to better comprehend the ash deposition problems.

Firstly, coal is heterogeneous. The mineral matter in coal is dependent on coal type and region. It is therefore important to characterise the mineral matter in a new or not well-researched coal in order to comprehend the ash deposition problems. The Zhundong lignite is of particular concern. Zhundong lignite, with an estimated reserve of up to 3.9 Gt, is a super-large energy resource in northwest China (Luguang et al. 2011; Shouyu et al. 2013) and is predicted by some to provide China with a secure energy supply for many decades to come. During combustion of Zhundong lignite, severe ash fouling and slagging are incurred in boilers due to high alkali and alkali earth metal (AAEM) content (Xu et al. 2013). However, ash deposition and deposition mitigation during combustion of high sodium and calcium Zhundong lignite is less understood, and the control and mitigation strategies on ash deposition of Zhundong lignite are also scarce. Therefore, understanding the ash transformation mechanisms and devising effective means to control and mitigate ash deposition during combustion of Zhundong lignite are essential for the utilization of Zhundong lignite.

Secondly, the effect of coal blending on ash deposition and mineral transformation is complex and unpredictable, even though coal blending is widely used to manage ash deposition. In particular, the mineral interactions between different coals may occur, possibly resulting in totally different ash properties and deposit behaviour from their source coals. Therefore, mineral transformation and ash deposition behaviour during combustion of blended coals is still required to gain an understanding of the effect of coal blending on ash deposition.
Based on the above analysis, the specific objectives of this study are also developed:

- To characterize the mineralogy, ash fusion temperature, and sintering temperature of the low temperature and high temperature coal ashes; delineate the effect of blending on ash fusibility, sintering and mineral transformations;
- To investigate the effect of coal blending and blending ratio on deposit properties; delineate the mechanism of ash deposition during combustion of coal blends in subcritical boilers;
- To investigate the effect of probe temperature on deposit properties; delineate the mechanism of ash deposition during combustion in SC/USC boilers;
- To identify the mechanisms of mineral interactions of coal blends;
- To investigate the effect of coal blending, water washing, and additives on ash fouling and slagging of Zhundong lignite
Chapter 3 Methodology, Techniques and Approach

In order to achieve the overall aims and the specific objectives, a series of experimental and analytical work was necessary. This chapter outlines the materials, the experimental equipment and the analytical instruments that were used in this research for the preparation and analysis of the coal samples, ash samples, and the ash deposit samples.

3.1 Materials

3.1.1 Coal samples

Three types of coal, namely, Australian bituminous (AB), Indonesian lignite (IL), and Zhundong lignite (ZL) with vastly different ash chemistry and ash mineralogy were chosen in this study. All coal samples were pulverised to particles with sizes less than 212 µm. The pulverised coal samples were then kept in a sealed container prior to use. The proximate and ultimate of coal samples and the chemistry of the ash prepared in muffle furnace in air at 815 ºC are shown in Table 3-1.

3.1.1.1 Preparation of coal blends

Coal blends were prepared to investigate the effect of blending of coals with vastly different mineralogy and inorganic constituents on the ash sintering, fouling, fusion and deposition characteristics. The pre-dried ZL and AB coal samples were blended with the weight percentage of AB (on dry weight base) in the blends being 20%, 40%, 50%, 60% and 80%, respectively. For convenience in subsequent discussion, the blends were denoted in a general form ZLxABy, with x and y indicating the weight percentages of ZL and AB in the blends, respectively. Likewise, coal blends between ZL and IL, IL and AB were also prepared and denoted as ZLxILy, and ILxABy, respectively, with x and y indicating their weight percentages in the blends.

3.1.1.2 Preparation of water washed coal

Water washed Zhundong lignite sample was also prepared to investigate the effect of water washing on the structure and chemistry of the Zhundong lignite ash deposits. The ZL coal sample with a size fraction between 50 - 100 µm was firstly mixed with deionised water at a concentration of 5 ml (water)/g (coal), which was then stirred at a speed of 100 rmp at 60 ºC for 24 hours to remove the water-soluble elements. The coal and water mixture was then filtered to separate the washed coal sample and the leachate.
The washed coal was then dried in an oven at 100°C for 24 hours to obtain the dried and washed Zhundong lignite.

### Table 3-1 Proximate and ultimate analysis of coal, and the chemistry of ash prepared in muffle furnace in air at 815 °C

<table>
<thead>
<tr>
<th></th>
<th>ZL</th>
<th>AB</th>
<th>IL</th>
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<tbody>
<tr>
<td><strong>Proximate analysis (wt% on dry base)</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ash</td>
<td>3.4</td>
<td>9.8</td>
<td>8.4</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>59.7</td>
<td>55.8</td>
<td>42.7</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>36.9</td>
<td>34.4</td>
<td>48.9</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>22.9</td>
<td>29.6</td>
<td>22.3</td>
</tr>
<tr>
<td><strong>Ultimate analysis (wt% on dry and ash free base)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>70.5</td>
<td>75.6</td>
<td>64.6</td>
</tr>
<tr>
<td>H</td>
<td>2.6</td>
<td>4.2</td>
<td>4.5</td>
</tr>
<tr>
<td>O</td>
<td>25.3</td>
<td>16.9</td>
<td>28.1</td>
</tr>
<tr>
<td>N</td>
<td>0.6</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>S</td>
<td>1.0</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>Ash composition (wt%)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>5.42</td>
<td>64.9</td>
<td>35.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.39</td>
<td>24.1</td>
<td>32.0</td>
</tr>
<tr>
<td>CaO</td>
<td>40.7</td>
<td>0.38</td>
<td>12.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.06</td>
<td>5.24</td>
<td>3.70</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.55</td>
<td>1.46</td>
<td>0.18</td>
</tr>
<tr>
<td>MgO</td>
<td>7.62</td>
<td>0.69</td>
<td>5.77</td>
</tr>
<tr>
<td>Na₂O</td>
<td>6.08</td>
<td>0.67</td>
<td>0.94</td>
</tr>
<tr>
<td>SO₃</td>
<td>26.9</td>
<td>0.22</td>
<td>4.24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.048</td>
<td>0.065</td>
<td>1.16</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.30</td>
<td>1.44</td>
<td>2.42</td>
</tr>
<tr>
<td>B/A ratio</td>
<td>4.79</td>
<td>0.19</td>
<td>0.34</td>
</tr>
</tbody>
</table>

### 3.1.1.3 Preparation of additive/coal mixtures

Kaolin and bauxite were used as additives to investigate the effect of additives on the deposit structure of Zhundong lignite. Kaolin was purchased from Sigma-aldrich with purity higher than 99% and sizes less than 10 µm. Bauxite was purchased from industry with sizes less than 100 µm and consisted of quartz (<3%), Kaolinite (1~20%), ferric
oxide (1~20%), and aluminum hydroxide (40~85%). The two additives were added into Zhundong lignite (with a size fraction between 50 - 100 \(\mu\)m) at weight ratios (relatively to coal) of 1%, 2%, and 4%, respectively, which was then vigorously stirred to prepare the additive/coal mixtures.

3.1.2 Preparation of ash samples
In this study, three types of ash samples prepared using different equipment subjected to different combustion temperatures were prepared. Firstly, low temperature ash (LTA) using plasma asher was prepared to identify the mineral matter in coal, which has been widely used in literature (Vassilev et al. 1995; Zhang, 2016). Secondly, ashes from muffle furnace in air atmosphere subjected to temperatures of 815 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C were prepared. Typically, the ash samples prepared at 815 °C were analysed for their chemical compositions, ash fusion temperatures, sintering temperatures, and mineral transformation. These analysis and characterisations permitted the investigation into the thermal behaviour of the mineral matter in coal during combustion, the sintering and fusion characteristics of the ash, and the effect of coal blending on these properties. Thirdly, the ash deposits formed on a probe at probe temperatures of 500 °C, 600 °C, 700 °C, and 750 °C, respectively, during combustion of coal samples in a drop tube furnace in air at 1400 °C were prepared, allowing analysis into the mineralogical, morphological and sintering characteristics of the ash deposits during combustion of the coal samples and coal blends, and shedding lights on the effect of coal blending on deposition behaviour and mechanisms.

3.2 Experimental equipment
3.2.1 Plasma asher
A K1050X Plasma asher was used to prepare the low temperature ash (LTA). The coal samples were firstly spread onto a tin plate, loaded to the plasma asher, and then ashed at ca.150 °C in oxygen atmosphere for 3 hours. During this ashing period, the top thin layer of the coal sample was able to be burnt, leaving the residue ash on the top. The residue of the sample was weighted, stirred, and ashed again for 3 hours until the weight of the residue was constant. The residue was then collected as the low temperature ash for the analysis of the mineral phases in coal.

3.2.2 Muffle furnace
A muffle furnace, as schematically shown in Figure 3-2, was also used to prepare the middle or high temperature ash samples. The coal samples were combusted in muffle
furnace in air atmosphere at temperatures of 815 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C for 2 hours. The residue of the sample was weighed and ashed again for 2 hours to measure the burnout rate of the coal samples. It was found that initial 2 hours’ ashing time in muffle furnace was sufficient to burn out the organic matter in the coal samples. The residue was thus collected and analysed for their mineral phases in coal, permitting investigation into the thermal behaviour of the coal (and coal blends) and the mineral transformations during combustion. In particular, the ash samples prepared in a muffle furnace at 815 °C were also analysed for their chemical composition, ash fusion temperatures and sintering temperatures.

Figure 3-1  A schematic of the plasma asher used for low temperature ash preparation

Figure 3-2  A schematic of the muffle furnace used for ash preparation
3.2.3 Drop tube furnace

A high temperature drop tube furnace (DTF), as schematically shown in Figure 3-3, was used in experimentation. The furnace consists of an electrically heated mullite tube of 2,000 mm in length and 55 mm in inner diameter. The DTF was preheated to a nominal operating temperature, being 1400 °C throughout this work. At this temperature, the temperature profile of the furnace was measured by sliding up and down a radiation-shielded S-type thermocouple and the results are shown in Figure 3-3. Note that there was an isothermal zone of about 800 mm in length at 1400 °C in the middle of the furnace. The dried coal sample was then fed into the furnace using a screw feeder at a feeding rate of 8-10 g h\(^{-1}\). Both primary air and secondary air were provided at a flow rate of 1 L min\(^{-1}\) to assist coal feeding and to ensure complete combustion, respectively. The Reynolds number was calculated to be 18.1, which indicated that the gas flow in the furnace was laminar.

Figure 3-3 A schematic of the drop tube furnace and a temperature profile along the centreline of the furnace when operating at 1,400 °C
An air-cooled cylindrical ash deposition probe with 32 mm outer diameter and 950 mm in length was vertically inserted into the furnace 400 mm from the bottom, as illustrated in Figure 3-4(a). The probe tip was situated at a position where the furnace temperature was 1000 °C. The temperature of the top surface of the probe was monitored with a K-type thermocouple attached to the back of the probe top surface and was controlled by adjusting the cooling air flow rate. During the experimentation, the temperature of the top surface was maintained at 500 °C, 600 °C, 700 °C, and 750 °C, to simulate superheaters in subcritical, supercritical and ultra-supercritical steam cycle boilers. Each experiment run typically lasted for more than 4 hours and at least 0.4 g ash at the probe top surface was collected. At the end of an experimental run, the probe was withdrawn from DTF, cooled to room temperature and the deposited ash recovered. By tilting the probe to a horizontal position, the loose ash particles on top surface would fall off and the remaining ash particles stuck on the surface was gently brushed off. The ash samples collected were analysed for their unburnt carbon contents in a thermogravimetric analyser (TGA) at 815 °C, the same temperature used for the proximate analysis, in air for 2 hours and the weight loss was found to be less than 3%, confirming that the combustion during the DTF experimentation was sufficiently complete.

![Diagram](image-url)

Figure 3-4  A schematic diagram of (a) the probe and (b) the removable top surface, and (c) the top view of a typical ash deposit on the top surface at 600 °C

In addition, the probe was also modified to have a removable probe surface as shown in Figure 3-4(b). The top surface of the probe was especially designed so that a removable disc with a thickness of 0.5 mm and a diameter of 25 mm was able to be fitted onto the probe top tip. The disc was made of HR3C alloy steel which is currently used as
superheater material in supercritical and ultra-supercritical boilers. After each run, the disc was removed from the probe top and the whole deposit on the disc was retained and kept intact for further analysis.

3.2.4 Pressure-drop sintering device
A pressure-drop sintering device, similar to that first introduced by Al-Otoom et al [17], was used to measure the ash sintering temperature, as schematically shown in Figure 3-5. An ash sample of about 0.4 g was firstly compacted into a pellet in-situ in a mullite tube (5 mm in ID) using a device, also as schematically shown in Figure 3-5, composed of a lever to exert a pressure on the ash pellet and a holder to support the mullite tube. Two copper rods with 5 mm in diameter were inserted into the tube to hold the ash pellet in a desired position at the centre of the mullite tube. At the end of the lever, a weight was hanged so that the ash pellet could be compacted.

![Figure 3-5](image)

Figure 3-5 A schematic of (a) the pressure-drop sintering device and (b) the pellet compaction device: 1 – furnace, 2 – ash pellet, 3 – thermocouple, 4 – pressure regulator, 5 – flowmeter, and 6 – pressure transducer

The mullite tube containing the ash pellet was then placed in a horizontal furnace and heated from room temperature at a rate of 6.7 °C min\(^{-1}\) in air. The air flow rate was maintained constant on the ash sintering temperature measurement. The upstream pressure in the mullite tube prior to the pellet was continuously recorded using a pressure transducer, and the temperature of the pellet was monitored with a thermocouple inserted from the downstream end of the tube to contact the pellet. The downstream pressure of the pellet was considered at the atmospheric pressure as it was opened to the atmosphere. The pressure drop across the pellet was thus equal to the gauge pressure in the mullite tube upstream of the pellet. The sintering temperature was determined by using a new criterion based on the first-order and second-order derivatives of the pressure drop curves as a function of temperature in accordance with
the literature (Li et al. 2016), as shown in Figure 3-6. The accuracy of this method is within ±12 °C, more accurate compared with other sintering temperature measurements (Al-Otoom et al. 2000; Jing et al. 2011). Each sample was also repeated twice to ensure a good repeatability and validity of the result.

Figure 3-6   A typical pressure drop curve as a function of temperature, and the first-order and second-order derivatives of the pressure drop curve

3.2.5 Ash fusibility analyser

An ash fusion temperature auto-analyser was used to determine the fusion temperatures of the ash samples prepared at 815 °C. The ash samples prepared at 815 °C were shaped into ash cones with a height of 20 mm. These ash cones were then heated in a horizontal furnace from room temperature to 900°C at a heating rate of 20 °C/min, and to 1500 °C at a heating rate of 5 °C/min in air atmosphere. The shapes of the ash cones during heating were continually monitored by an optical camera and were recorded at 5 minutes intervals. The fusion temperatures of the ash were determined by identifying the shapes of the cones. Four characteristic temperatures including deformation
temperature (DT), softening temperature (ST), hemisphere temperature (HT) and flow temperature (FT) were determined (Wall et al. 1998; Jing et al. 2013). Each sample was repeated three times to ensure a good repeatability of the results.

3.3 Analytical technique

3.3.1 X-ray Diffraction (XRD)

A Panalytical Empyrean X-Ray diffraction (XRD) with Cu Kα radiation was used to identify the mineralogy of the ash samples. The accelerating voltage and the current were 40 kV and 40 mA, respectively. Ash samples were 2θ scanned from 5° to 75° with a scanning rate of 5°/min. The mineral phases of the deposits were identified using “Search and Match” function in X’pert HighScore Plus software. In addition, the intensity of the characteristic peak of each mineral was recorded and used to indicate the content of each mineral phase in the ash (Qiu et al. 1999; Qiu et al. 1999; Jing et al. 2013). A high intensity of the characteristic peak represents a high concentration of this mineral phase in the ash, and vice versa.

3.3.2 Scanning Electron Microscope (SEM)

A Tescan Vega 3 scanning electron microscopy (SEM) coupled with energy dispersive X-Ray spectroscopy (EDS) was used to observe the morphology (size, shape, and particle sintering and melting) of the ash particles and to provide semi-quantitative spot elemental composition analysis of the ash/deposits. Two types of samples were prepared for surface and cross-section characterisation, respectively. The first type is surface characterisation. The coal ash sample was carefully scattered on double-sided adhesive carbon tape on a 10 mm diameter stub so that most of the particles could be observed individually. The other is cross-sectional characterisation. The ash deposits were embedded into epoxy resin, which were then cross-sectioned using a band saw and polished by using silicon carbide and finally using 1 µm gold paste. This sample preparation method allowed the structural and chemical variations of the ash deposit as a function of time or deposit thickness to be investigated. All samples were then carbon coated prior to SEM analysis.

During the analysis, secondary electrons (SE) or backscattered electrons (BSE) are used to image the surface of the sample. The energy dispersive X-ray spectrum is used to identify the elemental composition of the ash at selected spots in the sample.
3.3.3 XRF and ICP-AES analysis
X-ray Fluorescence (XRF) and ICP-AES were also used to determine the chemical composition of the coal ash samples.

3.3.4 Particle size analyser
The particle size distributions of the ash deposits were determined using a CILAS 1180 particle size analyser in aqueous mode, which is able to analyse particle sizes ranging from 0.04 μm to 2500 μm in size. The sizes of the ash particles in the deposits were characterised by D10, D50 and D90, the diameters at which the particles accounted for 10%, 50%, and 90% of the total particles (in volume) in the cumulative distribution curve, respectively.
Chapter 4 Characterisation of Ashes from Plasma Asher and Muffle Furnace

Coal is very heterogeneous, and the nature and mode of occurrence of the mineral matter in different coals also vary. Therefore, the ash deposition experienced in a boiler during combustion of different coals and coal blends may also be different. Thus, the identification of the key ash forming species in the coal and the understanding of their thermal behaviour during combustion is the first step to understand the roles of the mineral matter during ash deposition. Therefore, this chapter describes the investigation into the chemical and physical properties of coal ashes including ash mineralogy, ash sintering temperature, and ash fusibility characteristics, delineates the mineral transformation and interactions in the ash samples, and investigates the effect of coal blending on these properties.

4.1 Mineral matter in coal and low temperature ash

The XRD analysis on the coal samples and the low temperature ash (LTA) from plasma asher are shown in Figures 4-1 to 4-3. It is obvious that the mineral phases in the Australian bituminous (AB) coal and its LTA were quartz, kaolinite, and siderite. The mineral phases in the Indonesian lignite (IL) were dolomite, kaolinite and quartz with magnesium aluminium carbon hydrate presented in the LTA. However, there was no mineral phase identified in the Zhundong lignite (ZL), indicating that the mineral matter in the ZL were mainly included minerals or organically-bound elements. After ashing the ZL in the plasma asher, anhydrite, quartz, and sodium nitrate were identified in the LTA. The mineralogical difference between the ZL and its LTA indicates that these mineral phases in LTA were formed during low temperature ashing process, rather than the initial mode of occurrence in Zhundong lignite.

4.2 Characterisation of ash from muffle furnace

4.2.1 Ash chemistry

The proximate and ultimate analysis of coal samples, and the chemical composition of their ashes prepared in muffle furnace in air at 815 ºC according to Australian Standard 1038.4 have been shown in Table 3-1. It is obvious that the ZL ash was dominated by basic oxides (CaO, MgO, Na₂O, Fe₂O₃ and K₂O), with acidic oxides (SiO₂, Al₂O₃ and TiO₂) only accounted for a minor fraction, leading to a basic oxides to acidic oxides (B/A) ratio of 4.79, suggesting that its low ash fusion temperatures and high ash
deposition propensity (Raask 1985; Vassilev et al. 1996; Vassilev et al. 1996; Baxter 2000; Zhang 2013; Luan et al. 2014). In contrast, the AB and IL coal ashes were dominated by acidic oxides including SiO₂ and Al₂O₃, suggesting the abundance of silica, silicates, or aluminosilicate in the ash, and indicating relatively high ash fusion temperatures of the ash samples and low ash deposition propensity (Raask 1985; Luan et al. 2014).

Figure 4-1 XRD patterns of (a) the Australian bituminous and (b) its low temperature ash from Plasma asher. 1 – Quartz, 2 – Kaolinite, 3 – Silicon Oxide, 4 – Siderite, and 5 – Magnesium aluminium carbon hydrate

Figure 4-2 XRD patterns of (a) the Indonesian lignite and (b) its low temperature ash from Plasma asher. 1 – Kaolinite, 2 – Dolomite, 3 – Silicon Oxide, 4 – Quartz, and 5 – Magnesium aluminium carbon hydrate
Figure 4-3  XRD patterns of (a) the Zhundong lignite and (b) its low temperature ash.
1 – Calcium sulphate hydrate, 2 – Quartz, 3 – Calcium carbonate, 4 – Sodium nitrate, 5 – anhydrite, 6 – Magnesium Silicate Hydroxide, and 7 – Ammonium Aluminum Phosphate Hydrate

The above analysis has provided valuable information for prediction or evaluation ash deposition behaviour of different coals during combustion in power plants. However, the B/A ratio is not the only index that being used for prediction of ash deposition. Different indexes shown in Tables 4-1 and 4-2 could be used as alternatives to predict ash slagging and fouling during combustion. Basically, it is obvious that the AB coal has low slagging propensity, but its fouling propensity is hard to be evaluated according to the indexes shown in Table 4-2. The IL ash shows high or medium slagging propensities, and moderate fouling propensity. However, the ZL ash has high to severe slagging and fouling propensities.

Table 4-1  Prediction of the slagging propensity of the coal ash samples

<table>
<thead>
<tr>
<th>Index</th>
<th>AB</th>
<th>Propensity</th>
<th>Value</th>
<th>Propensity</th>
<th>Value</th>
<th>Propensity</th>
<th>Value</th>
<th>Propensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>B/A</td>
<td>0.09</td>
<td>Low</td>
<td>0.35</td>
<td>High</td>
<td>4.79</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica ratio</td>
<td>91</td>
<td>Low</td>
<td>61</td>
<td>High</td>
<td>9.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphur content</td>
<td>0.02</td>
<td>Low</td>
<td>1.49</td>
<td>Medium</td>
<td>128.9</td>
<td>severe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fusibility (°C)</td>
<td>1380</td>
<td>Low</td>
<td>1302</td>
<td>Medium</td>
<td>1127</td>
<td>severe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>%Fe₂O₃</td>
<td>5.24</td>
<td>Low</td>
<td>3.70</td>
<td>Low</td>
<td>3.06</td>
<td>low</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃/CaO</td>
<td>13.8</td>
<td>Low</td>
<td>0.29</td>
<td>High</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4-2 Prediction of the fouling propensity of the coal ash samples

<table>
<thead>
<tr>
<th>Index</th>
<th>AB</th>
<th>Propensity</th>
<th>IL</th>
<th>Propensity</th>
<th>ZL</th>
<th>Propensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B/A)(%Na)</td>
<td>0.06</td>
<td>Low</td>
<td>0.33</td>
<td>Medium</td>
<td>29.4</td>
<td>Severe</td>
</tr>
<tr>
<td>%Na₂O</td>
<td>0.67</td>
<td>Medium</td>
<td>0.94</td>
<td>Medium</td>
<td>6.08</td>
<td>high</td>
</tr>
<tr>
<td>Σ(%Na₂O +0.6589 %K₂O)</td>
<td>1.63</td>
<td>High</td>
<td>1.05</td>
<td>Low</td>
<td>6.44</td>
<td>high</td>
</tr>
</tbody>
</table>

Effect of coal blending on ash chemistry

The effect of coal blending on ash chemistry was also investigated. The chemical composition of the blended coal ash samples and their corresponding basic to acidic ratio are calculated and shown in Table 4-3. This calculation is based on the blending ratio and the ash contents of their parent coals, assuming that there are no chemical reactions at 815 ºC during ashing process (Qiu et al. 1999; Qiu et al. 1999). It is clear that the chemistry of the ash and its B/A ratio vary with the coal type and the blending ratio. For ZL and AB blends, the B/A ratio decreased from 0.72 to 0.14 as the AB ratio in the blends increased from 20% to 80%, indicating that the ash slagging propensity of the ZL coal would be mitigated (Zhang 2013). Of particular concern is that the Na content (in the form of Na₂O) decreased as the AB ratio in the blends increased, suggesting that the fouling propensity of the coal blends would also be mitigated (Degereji et al. 2012). Similar trends were also applied for the ZL and IL blends that the B/A ratio and the Na content decreased as the IL ratio in the blends increased. For IL and AB blends, their B/A ratio varied in a narrow range from 0.12 to 0.26 with Na content (in the form of Na₂O) varying from 0.71 to 0.87, indicating that the deposition propensity of these blends was low and the effect of coal blending on ash deposition might be less significant (Bryers 1996). Note that this calculation might to some degree underestimate the B/A ratio of the ash and therefore underestimate the slagging and fouling propensity of the ash. This is because, without coal blending, the vaporisation of Na occurred during ashing of Zhundong lignite (Zhang et al. 2015), while the addition of AB or IL coal into Zhundong lignite would retain the Na due to the presence of silica or silicate the blends, leading to even higher Na content in the coal ash samples than the calculated value (Bryers 1996).
4.2.2 Ash mineralogy

The chemistry of the ash represents the basic chemical composition of the ash in the forms of oxides. However, the actual mode of occurrence of the inorganic elements in the ash is more than oxides. Therefore, XRD analysis was performed to investigate the forms of the inorganic elements, i.e., the mineral phases, in the ash.

Figure 4-4 shows the XRD patterns of the AB, ZL, and IL ash samples. Quartz was found to be the dominant mineral phase in the AB ash, while hematite, titania (TiO$_2$), and sodium iron oxide (NaFeO$_2$) were among the minor mineral phases (Jing et al. 2013; Jing et al. 2013). Quartz is one of the main refractory minerals inhibiting the formation of low-melting point eutectics and therefore increasing ash fusion temperature and sintering temperature, and decreasing ash deposition propensity (Zhou et al. 2015). The ZL ash was rich in anhydrite, periclase, yeelimite (Ca$_4$Al$_6$O$_{12}$SO$_4$), lime, cristobalite, calcium silicate (Ca$_2$SiO$_4$), and magnesite. These mineral phases have low-melting points and are able to form low-melting point eutectics at a lower temperature, thus increasing ash sintering the deposition propensity (Zhou et al. 2015). For the IL ash, only quartz and anhydrite were identified as the minor mineral phases, implying that most of the inorganic elements existed as amorphous or glass phases in the IL ash.

Figure 4-4 XRD patterns of the AB, ZL, and IL ash samples. 1 – Quartz, 2 – Hematite, 3 – Titanium Oxide, 4 – Sodium Iron Oxide (NaFeO$_2$), 5 – Anhydrite, 6 – Periclase, 7 – Yeelimite, 8 – Lime, 9 – Calcium silicate, and 10 – Silicon oxide.
## Table 4-3 The calculated chemical composition of the blended coal ash samples

<table>
<thead>
<tr>
<th>Coal blends</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>B/A ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZL80AB20</td>
<td>33.03</td>
<td>14.61</td>
<td>21.99</td>
<td>4.07</td>
<td>0.97</td>
<td>4.40</td>
<td>3.57</td>
<td>14.52</td>
<td>0.06</td>
<td>0.83</td>
<td>0.72</td>
</tr>
<tr>
<td>ZL60AB40</td>
<td>46.93</td>
<td>18.75</td>
<td>12.56</td>
<td>4.58</td>
<td>1.19</td>
<td>2.78</td>
<td>2.30</td>
<td>8.28</td>
<td>0.06</td>
<td>1.10</td>
<td>0.35</td>
</tr>
<tr>
<td>ZL50AB50</td>
<td>51.58</td>
<td>20.13</td>
<td>9.41</td>
<td>4.75</td>
<td>1.26</td>
<td>2.24</td>
<td>1.88</td>
<td>6.20</td>
<td>0.06</td>
<td>1.18</td>
<td>0.27</td>
</tr>
<tr>
<td>ZL40AB60</td>
<td>55.30</td>
<td>21.24</td>
<td>6.89</td>
<td>4.89</td>
<td>1.31</td>
<td>1.81</td>
<td>1.54</td>
<td>4.53</td>
<td>0.06</td>
<td>1.26</td>
<td>0.21</td>
</tr>
<tr>
<td>ZL20AB80</td>
<td>60.90</td>
<td>22.91</td>
<td>3.09</td>
<td>5.09</td>
<td>1.40</td>
<td>1.16</td>
<td>1.03</td>
<td>2.02</td>
<td>0.06</td>
<td>1.36</td>
<td>0.14</td>
</tr>
<tr>
<td>IL20AB80</td>
<td>60.06</td>
<td>25.38</td>
<td>2.38</td>
<td>4.99</td>
<td>1.25</td>
<td>1.51</td>
<td>0.71</td>
<td>0.87</td>
<td>0.24</td>
<td>1.60</td>
<td>0.12</td>
</tr>
<tr>
<td>IL40AB60</td>
<td>54.73</td>
<td>26.79</td>
<td>4.57</td>
<td>4.72</td>
<td>1.02</td>
<td>2.42</td>
<td>0.76</td>
<td>1.59</td>
<td>0.44</td>
<td>1.77</td>
<td>0.16</td>
</tr>
<tr>
<td>IL50AB50</td>
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<td>27.54</td>
<td>5.75</td>
<td>4.57</td>
<td>0.90</td>
<td>2.91</td>
<td>0.79</td>
<td>1.97</td>
<td>0.54</td>
<td>1.87</td>
<td>0.18</td>
</tr>
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<td>28.34</td>
<td>7.00</td>
<td>4.41</td>
<td>0.77</td>
<td>3.42</td>
<td>0.81</td>
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<td>1.97</td>
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<tr>
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<td>30.07</td>
<td>9.69</td>
<td>4.08</td>
<td>0.49</td>
<td>4.53</td>
<td>0.87</td>
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<td>0.89</td>
<td>2.18</td>
<td>0.26</td>
</tr>
<tr>
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<td>0.40</td>
<td>6.88</td>
<td>4.02</td>
<td>17.81</td>
<td>0.49</td>
<td>1.15</td>
<td>1.26</td>
</tr>
<tr>
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<td>22.81</td>
<td>22.75</td>
<td>3.47</td>
<td>0.31</td>
<td>6.43</td>
<td>2.79</td>
<td>12.37</td>
<td>0.76</td>
<td>1.66</td>
<td>0.73</td>
</tr>
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<td>20.31</td>
<td>3.53</td>
<td>0.28</td>
<td>6.27</td>
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<td>0.86</td>
<td>1.84</td>
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<tr>
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<td>6.14</td>
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<td>8.76</td>
<td>0.94</td>
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<tr>
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<td>0.21</td>
<td>5.93</td>
<td>1.38</td>
<td>6.17</td>
<td>1.07</td>
<td>2.24</td>
<td>0.41</td>
</tr>
</tbody>
</table>
ZL and AB blends: The XRD patterns of the ash samples of the ZL and AB blends are shown in Figure 4-5. It is obvious that coal blending has significant effect on the ash mineralogy. For individual ZL ash, anhydrite, periclase, yeelimite (Ca$_4$Al$_6$O$_{12}$SO$_4$), lime, cristobalite, calcium silicate (Ca$_2$SiO$_4$), and magnesite were identified in the ash as shown in Figure 4-4. As the AB ratio in the blends increased to 20%, nepheline and hauyne were identified in the ZL80AB20 ash sample while Ca-bearing mineral phases including yeelimite, lime, and calcium silicate decreased. This is because the total Ca contents in the coal blend decreased, leading to the absent formation of yeelimite, lime and calcium silicate in the ash. For Na, however, the formation of nepheline and hauyne indicates that Na had been captured by silica and silicate from the AB coal. At the AB ratio of 40%, nepheline was still identified in the ZL60AB80 blend. As the AB ratio further increased, the remaining mineral phases in the ash were quartz, anhydrite, hematite, sodium iron oxide, and titanium oxide. This means that the formation of nepheline and hauyne were inhibited as the AB ratio in the blends further increased. Meanwhile, the peak intensity of quartz increased as the AB ratio increased, indicating that the quartz content in the ash increased. Likewise, the content of anhydrite decreased as the AB ratio increased as indicated by its peak intensity. These indicate that the ash sample became more refractory as the AB ratio increased, therefore low slagging and fouling propensity of the ash are expected.

Figure 4-5  XRD patterns of the ash samples of ZL and AB blends. 1 – Quartz, 2 – anhydrite, 3 – Nepheline, 4 – Hematite, 5 – Hauyne, 6 – Sodium Iron Oxide (NaFeO$_2$), 7 – Titanium Oxide
**ZL and IL blends:** The XRD patterns of the ash samples of the ZL and IL blends are shown in Figure 4-6. It is obvious that the mineral phases in the ash vary with the blending ratio. For ZL80IL20 coal ash, anhydrite, quartz, nepheline, sodium aluminium silicate, and potassium aluminium silicate were identified. Among these mineral phases, nepheline, sodium aluminium silicate and potassium aluminium silicate were not identified in both the ZL and IL coal ash samples, indicating that mineral interactions had occurred in the ZL80IL20 ash sample. As the IL ratio in the coal blends further increased, the formation of nepheline, sodium aluminium silicate and potassium aluminium silicate was inhibited due to the increasing amount of silicates and decreasing amount of alkali in the ash (Table 4-3). As a result, the mineral phases in the ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 ash samples were anhydrite, quartz, and hematite.

**IL and AB blends:** Figure 4-7 shows the XRD patterns of the ash samples of the IL and AB blends. It is clear that the mineral phases in these ash samples were quite similar, with quartz, hematite, sodium iron oxide and anatase, and anhydrite being dominant mineral phases. Moreover, as the AB ratio increased, the peak intensity of quartz increased, indicating that the quartz content in the ash increased as the AB ratio increased.

![XRD patterns of the ash samples of the ZL and IL blends](image)
To be summary, the mineral phases in the ash vary with the coal type and the blending ratio. For ZL coal ash, fluxing minerals such as anhydrite, periclase, yeelimite, and calcium silicate dominated the ZL ash, indicating that the ZL ash has low melting points and thus high deposition propensity. The AB and IL ash, however, were dominant by refractory mineral phases including quartz, indicating that these coal ash samples have low deposition propensity. For coal blends, the major mineral phases in the ash such as quartz and anhydrite were still identified in the blended coal ash samples, yet the contents of these mineral phases vary with the blending ratio as indicated by their peak intensities. Moreover, nepheline and/or hauyne were found in the ZL80AB20 and ZL80IL20 ash samples, indicating that mineral interactions have occurred in the blended coal ash samples. As AB or IL coal in the blends further increased, the formation of nepheline and hauyne was absent, indicating that the further addition of AB or IL coal inhibited the formation of fluxing minerals.

![Figure 4-7 XRD patterns of the ash samples of the IL and AB blends, 1 – Quartz, 2 – Hematite, 3 – Anatase (TiO\textsubscript{2}) and anhydrite, 4 – Sodium Iron Oxide (NaFeO\textsubscript{2})](image)

**4.2.3 Ash sintering temperature**

Sintering temperature refers to the bonding or welding of adjacent particles, which is a main mechanism for strength development of the ash deposits (Al-Otoom et al. 2000). For ash deposition in pulverised coal-fired boilers, once the outer surface temperature of the deposit on surfaces reaches the sintering temperature, the particles in that layer will become sticky and sintered, progressively forming sintered, semi-fused and fused...
deposit (Zhang 2013). The low-melting point eutectics will be formed and the possibilities of mineral interactions will increase. Therefore, ash sintering temperature is regarded as a significant criterion for the evaluation of ash deposition propensity (Luan et al. 2014).

Table 4-4 shows the sintering temperatures of the ash and the effect of coal blending on ash sintering temperature. It is obvious that the sintering temperature of ZL ash was the lowest at 748 °C, indicating that the ZL ash had relatively high sintering tendency. The AB and IL ash samples, however, had higher ash sintering temperatures, indicating relatively low sintering tendency and deposition propensity of the ash. For ZL and AB blends, sintering temperature of the ash gradually increased as the ratio of AB increased, indicating that the sintering tendency of the ash decreased. Similar trend was also applied for the ZL and IL blends as the ratio of IL in the coal blends increased.

The difference in ash sintering temperature was related to the difference in chemistry and the mineralogy of the ash as described above. The sintering temperature as a function of the B/A ratio was plotted and shown in Figure 4-8. It can be seen that the sintering temperature decreased as the B/A ratio increased. For the ZL and AB blends, the sintering temperature significantly decreased as the B/A ratio increased from 0.09 to 4.79. A similar trend was also observed for the ZL and IL blends whose ash sintering temperatures significantly decreased as the B/A ratio increased from 0.34 to 4.79. For the AB and IL blends, the sintering temperature also decreased as the B/A ratio increased from 0.09 to 0.34. These results are consistent with the findings by Luan et al (Luan et al. 2014) that the ash sintering temperature (determined using the old criterion) decreases with increasing the B/A ratio. In addition, it was observed that the sintering temperature dropped very significantly at low B/A ratio (10-20%) but decreased slowly afterwards. This is because at low B/A ratios, silica or aluminium silicate dominated the bulk ash. As the B/A ratio was increased, more alkali and alkali earth contents were present in the ash and this portion of low melting-point fluxing minerals or eutectics would significantly induce sintering and sharply decrease the ash sintering temperature. At high B/A ratios, the ash sintering temperature still decreased but at a slower rate as a significant amount of alkali and alkali earth contents that were responsible for sintering had already existed in the ash.
However, B/A ratio was not the only factor that determines the sintering temperature. Other factors such as the ash geochemistry, mineralogy and alkali and alkali-earth content also play a significant role. For example, with similar B/A ratios, the sintering temperature of the ZL60AB40 blend coal ash (B/A = 0.35) was much lower than that of the IL ash (B/A = 0.34), as shown in Figure 4-8. This is due to the difference in the sodium content in the ash and the mineralogy of the ash. First of all, according to the XRF analysis, the ZL60AB40 blend coal ash has a content of Na₂O of 2.30%, which was higher than that in the IL ash (0.94%), as shown in Table 3-1 and Table 4-3, respectively. The abundance of sodium is believed to enhance the sintering of ash particles and decrease the ash sintering temperature (Raask 1985; Zhang 2013). In addition, the XRD results show that quartz, anhydrite, hematite, and nepheline (Na₃K(Si₀.₅₅₃Al₀.₄₄₇)₆O₁₆) were identified in the ZL60AB40 blend coal ash, while only quartz and anhydrite were identified in the IL ash. Both hematite and nepheline are fluxing minerals and are able to form low melting-point eutectics (Raask 1985; Zhang 2013). As a result, the sintering temperature of the ZL60AB40 blend coal ash was much lower than that of the IL ash.

Table 4-4 Sintering temperatures of the ashes of the coal blends prepared in the muffle furnace at 815 °C

<table>
<thead>
<tr>
<th>ZL and AB blends</th>
<th>Ts (°C)</th>
<th>ZL and IL blends</th>
<th>Ts (°C)</th>
<th>IL and AB blends</th>
<th>Ts (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZL</td>
<td>748</td>
<td>ZL</td>
<td>748</td>
<td>AB</td>
<td>938</td>
</tr>
<tr>
<td>ZL80AB20</td>
<td>775</td>
<td>ZL80IL20</td>
<td>764</td>
<td>AB80IL20</td>
<td>904</td>
</tr>
<tr>
<td>ZL60AB40</td>
<td>807</td>
<td>ZL60IL40</td>
<td>826</td>
<td>AB60IL40</td>
<td>888</td>
</tr>
<tr>
<td>ZL50AB50</td>
<td>817</td>
<td>ZL50IL50</td>
<td>836</td>
<td>AB50IL50</td>
<td>878</td>
</tr>
<tr>
<td>ZL40AB60</td>
<td>826</td>
<td>ZL40IL60</td>
<td>846</td>
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<td>938</td>
<td>IL</td>
<td>875</td>
<td>IL</td>
<td>875</td>
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</table>
4.2.4 Ash fusion temperatures

The fusibility of the ash was also analysed and the effect of coal blending investigated. Table 4-5 shows the measured ash fusion temperatures (DT, ST, HT and FT) of the coal blends. It is obvious that the AB ash, with DT at 1350 °C and ST higher than 1500 °C, had relatively high fusion temperatures. Likewise, the IL ash had DT at 1253 °C and ST higher than 1500 °C. These indicate that both AB and IL coal ashes were refractory and had low melting and fusion propensity (Qiu et al. 1999; Qiu et al. 1999). The ZL ash, however, had relatively low ash fusion temperatures with DT at 1070 °C and ST at 1273 °C, indicating that ZL ash has relatively high melting propensity and thus high slagging propensity (Qiu et al. 1999; Qiu et al. 1999).

ZL and AB blends: Table 4-5 also shows the fusion temperatures of the ash of the ZL and AB blends. It is clear that the ash fusion temperatures were dependent on blending ratio and did not follow the same trend. The DT increased as ratio of AB in the blends increased, suggesting that the AB coal would inhibit the initial deformation of ZL ash. The ST, HT, and FT, however, were not always increased. When the ratio of AB was 40%, the ST, HT, and FT were the lowest at 1219 °C, 1229 °C, and 1253 °C respectively. As the ratio of AB increased to 50% and even higher, the ST and FT of the ash increased. This means that the AB coal ash, which is abundant in acidic oxides.
(particularly SiO$_2$) with high ash fusion temperatures, was not always effective in elevating fusion temperatures of the ZL ash, consistent with the literature that the addition of SiO$_2$ at low levels promoted the melting of ZL ash (Zhou et al. 2015). The mineral interactions in the ash had occurred, leading to the formation of new mineral phases or eutectics and thus diverse relationship between ash fusion temperatures and the blending ratio (Qiu et al. 1999; Qiu et al. 1999; Bryant et al. 2000; Pang et al. 2013; Xu et al. 2015).

Table 4-5  Ash fusion temperatures of blended coals under air atmosphere

<table>
<thead>
<tr>
<th>Samples</th>
<th>DT (°C)</th>
<th>ST (°C)</th>
<th>HT (°C)</th>
<th>FT (°C)</th>
</tr>
</thead>
<tbody>
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<td>&gt;1500</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
</tr>
<tr>
<td>IL</td>
<td>1253</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
</tr>
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<tr>
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<td>1406</td>
<td>1441</td>
<td>1478</td>
</tr>
<tr>
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<td>1383</td>
</tr>
<tr>
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<td>1386</td>
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<tr>
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<td>&gt;1500</td>
<td>&gt;1500</td>
<td>&gt;1500</td>
</tr>
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</table>

**ZL and IL blends:** The effect of IL coal on the fusion temperatures of the ZL ash are also shown in Table 4-5. It is obvious that both DT and ST increased as the ratio of IL in the ZL and IL blends increased. The FT, however, decreased first as the ratio of IL
increased to 20%, and then increased afterwards. Compared to the FTs of the ash from ZL and AB coal blends, the significant drop in FT as a function of IL ratio was not observed in the ZL and IL blends, indicating that the IL coal was more effective in elevating fusion temperatures of ZL ash than the AB coal. The difference in ash mineralogy of the IL and AB coal as discussed above are responsible for the variations in ash fusion temperatures.

**IL and AB blends:** For IL and AB blends, their ash fusion temperatures maintained at relatively high temperatures with DT higher than 1290 °C and ST higher than 1500 °C, indicating high ash fusion temperatures and thus low slagging propensity of the ash. This is consistent with their ash chemistry and mineralogy as analysed above.

### 4.2.5 Mineral transformation

The analysis on the chemistry, mineralogy, sintering temperature, and fusion temperatures of the ash samples have provided detailed information on the ash properties, allowing analysis into the effect of coal blending on these properties and on ash deposition propensities. However, all the ash samples were prepared at one ashing temperature at 815 °C, which is not sufficient to investigate thermal behaviour of the mineral matter in coal and the effect of coal blending on mineral transformation and interactions at higher temperatures. To achieve this aim, ash samples prepared at temperatures of 815 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C were analysed using XRD for their mineralogy. The identified mineral phases in the ash samples are shown in Tables 4-6 and 4-7. The intensity variations of the major mineral phases are also recorded and shown in Figures 4-9 to 4-13 to illustrate the variation in the contents of the mineral phases in the ash samples.

**ZL ashes:** Figure 4-9 shows the variations in mineral phases of the ZL ash, AB ash and the IL ash as a function of ashing temperature. The mineral phases in the ZL ash at 815 °C, as shown in Figure 4-9(a), were identified as anhydrite, periclase, yeelimite, calcite, calcium silicate, and cristobalite, with anhydrite being the dominant mineral phase with the highest peak intensity. The abundant of fluxing minerals and the absent of refractory minerals explain the low sintering temperature as mentioned above. At 900 °C, the peak intensity of calcite diminished while lime was identified in the ash, suggesting that calcite had decomposed to lime at 900 °C. As ashing temperature further increased, the peak intensities of anhydrite, cristobalite, and lime decreased, whereas the peak
intensities of calcium silicate and yeelimite increased, suggesting that anhydrite and lime had reacted with other minerals to form yeelimite and calcium silicate. In addition, the amount of periclase increased as ashing temperature increased, indicating that periclase might be relatively stable than lime and anhydrite and therefore was not involved into the mineral interactions. These Ca-bearing minerals such as anhydrite, yeelimite, calcium silicate had low melting points (Bryers 1996; Zhang 2013; Panagiotidis et al. 2015), and that is why the ash fusion temperatures of ZL coal were low. It is also worth noting that Na-bearing minerals were not identified in the ash at 815 °C even though its amount was considerable (Na₂O=6.08%), indicating that Na existed as amorphous phase or glass phase in the ash. As ashing temperature increased, Na would evaporate and could not be retained in the ash due to the absence of Na-absorbing silica or aluminium silicate in the ash (Dong et al. 2015; Li et al. 2015; Wang et al. 2015; Yuan et al. 2015; Zhang et al. 2015; Zhou et al. 2015; Zhou et al. 2015), therefore resulting in the absence of Na-bearing minerals in the ash at high temperatures.

**AB ashes:** Figure 4-9(b) shows the mineral phases in the AB ash as a function of ashing temperature. At 815 °C, quartz, hematite, titanium oxide, and sodium iron oxide were identified in the AB ash, with quartz being the dominant mineral phase, leading to high ash sintering temperature. As ashing temperature increased, the peak intensities of these mineral phases decreased, suggesting that these mineral phases had incorporated into other minerals or eutectics. Meanwhile, mullite was formed at 1100 °C and its content further increased as ashing temperature increased to 1200 °C. The presence of refractory minerals such as mullite and quartz with high melting points (Raask 1985; Baxter 2000; Bryant et al. 2000; van Dyk 2006; Song et al. 2009; Xu et al. 2015), explains the high fusion temperatures of the AB coal ash.

**IL ashes:** Figure 4-9(c) shows the mineral phases in the IL ash as a function of ashing temperature. At 815 °C, quartz, anhydrite, and anatase were identified in the IL ash. As ashing temperature increased, these minerals gradually decreased. Meanwhile, mullite was identified at 1000 °C, and became the dominant mineral phase at 1200 °C. In addition, anorthite was formed at 1100 °C and 1200 °C, suggesting that the interactions between Ca and aluminium silicate occurred in the ash. The abundance of mullite would explain why the IL coal ash had relatively high fusion temperatures.
Figure 4-9  Variations in the main mineral phases of the (a) ZL ash, (b) AB ash, and (c) IL ash as a function of ashing temperature.
Figure 4-10 Variations in the main mineral phases of the (a) ZL80AB20 ash, (b) ZL60AB40 ash, and (c) ZL50AB50 as a function of ashing temperature.
**ZL80AB20 ashes:** Figure 4-10 and Figure 4-11 present the mineral phases in the ash of ZL and AB blends at different ashing temperatures. As shown in Figure 4-10(a), the mineral phases in the ZL80AB20 ash at 815 ºC were identified as anhydrite, quartz, hematite, nepheline, and hauyne with anhydrite and quartz being dominant minerals. Among these mineral phases, Na-bearing minerals nepheline and hauyne were not identified in both the ZL ash and AB ash, suggesting that mineral interaction between ZL and AB coal ash occurred. As ashing temperature increased to 900 ºC, the amount of anhydrite, quartz, hematite, and nepheline decreased, whereas the amount of hauyne increased, indicating that mineral interaction between quartz, and Na and Ca occurred. Meanwhile, diopside sodian and akermanite were formed at 900 ºC, indicating that mineral interaction between quartz, lime and periclase occurred. At 1000 ºC, the amount of anhydrite, and nepheline, and akermanite diminished, and quartz decreased to minor amount, suggesting that these mineral phases had transformed into other minerals or eutectics. Furthermore, the amount of hauyne and hematite were relatively stable. In addition, akermanite-gehlenite and wollastonite were formed at 1000 ºC. As ashing temperature further increased to 1100 ºC, the remaining minerals in the ash were akermanite-gehlenite and wollastonite, suggesting that the interactions between Ca and silicate had occurred. Nepheline, hauyne, and gehlenite had even lower melting points than those in the ZL ash (Zhou et al. 2015), and this is why the fusion temperatures of the ZL80AB20 ash were lower than those of the ZL100 ash. This means that the AB coal ash, which was rich in refractory minerals particularly quartz, would promote the melting of ZL ash at ZL80AB20.

**ZL60AB40 and ZL50AB50 ashes:** Figure 4-10(b) and Figure 4-10(c) illustrate the variations in the mineral phases in the ZL60AB40 and the ZL50AB50 ash at all ashing temperatures, respectively. It is clear that the mineral phases in the ashes became less complex as the AB ratio increased. At 815 ºC, the major mineral phases in the ZL60AB40 and ZL50AB50 ashes (Table 4-6) were quartz and anhydrite, with Na-bearing minerals accounted for only minor fraction, indicating that the formation of fluxing mineral was inhibited. Meanwhile, as the AB ratio increased from 20% to 50%, the peak intensity of quartz increased while the peak intensity of anhydrite decreased, indicating that the ash became more refractory. As ashing temperature increased, the fates of the existing minerals including anhydrite, quartz, and hematite in the ash were similar to those in ZL80AB20 ash. In particular, for ZL60AB40 ash, anorthite was formed at 1000 ºC, and akermanite and augite were formed at 1100 ºC, indicating the
interactions between calcium and aluminium silicate occurred in the ash. In addition, the amount of hauyne was comparably less than that in the ZL80IL20, suggesting that the formation of hauyne was inhibited. For ZL50AB50 ash, nepheline was not identified in the ash at 815 °C, and hauyne was not identified at all ashing temperatures, suggesting that the formation of Na-bearing minerals was inhibited. This also explains why the fusion temperatures of the ZL50AB50 ash were higher than those of the ZL60AB40 ash.

**ZL40AB60 and ZL20AB80 ashes:** Figure 4-11(a) and Figure 4-11(b) illustrate the variations in the mineral phases in the ZL40AB60 and the ZL20AB80 ash at all ashing temperatures. It is obvious that the mineral phases in the ash samples became less complex than the other ZL and AB blends. At 815 °C, anhydrite, quartz, hematite, rutile, and sodium iron oxide were identified in the ZL40AB60 ash and ZL20AB80 ash with quartz being dominant mineral phase. The intensity of refractory mineral quartz further increased while the intensity of anhydrite decreased as the ratio of AB in the coal blends increased. This explains why the sintering temperature of the ash further increased as the AB ratio in the coal increased. At the temperature increased to 900 °C, sodium iron oxide and rutile disappeared. In addition, anorthite was formed at 900 °C in the ZL40AB60 ash, and at 1100 °C in the ZL20AB80 ash, suggesting that the interaction between Ca and aluminium silicate occurred, but was delayed as the AB ratio increased. Moreover, mullite was exclusively identified in the ZL40AB60 and ZL20AB80 ashes at 1100 °C and above, other than ZL80AB20, ZL60AB40, and ZL 50AB50 ash. Meanwhile, the Na-bearing minerals including nepheline and hauyne were not identified. The formation of refractory mineral mullite and the absence of fluxing minerals nepheline and hauyne explain why the fusion temperatures of the ash samples increased as the amount of AB further increased.

Summarising the evidence discussed above, for ZL and AB coal blends, Na-bearing minerals such as nepheline and hauyne were identified in the ZL80AB20, ZL60AB40, and ZL50AB50 blends ash whereas refractory minerals such as quartz and mullite were absent. These Na-bearing minerals have even lower melting points than the Ca-bearing minerals, and therefore decreasing the ash fusion temperatures including ST and FT. In other words, the AB ash, promoted the melting of Zhundong lignite ash when the ratio of AB in the blends was less than 50%. As the amount of AB in the blends further increased, mullite was formed in the ash while the formation of Na-bearing fluxing minerals was inhibited, leading to the increase in ash fusion temperatures.
ZL80IL20 ashes: Figures 4-12 and 4-13 exhibit the variations in the mineral phases in the ashes of ZL and IL blends. The mineral phases in the ZL80IL20 ash at 815 °C, as shown in Figure 4-12(a), were identified as anhydrite, quartz, nepheline, sodium aluminium silicate, and potassium aluminum silicate with anhydrite being the dominant mineral phase. Among these mineral phases, nepheline was not identified in both ZL and IL ashes, indicating that the interactions between Na in the ZL coal ash and silicate in IL coal ash occurred. As ashing temperature increased to 900 °C, the amount of anhydrite, quartz, sodium aluminium silicate, and potassium aluminum silicate decreased, indicating that these minerals had decomposed or incorporated into other minerals or eutectics. In addition, hauyne was formed in the ash at 900 °C. At 1000 °C, gehlenite, nepheline, hauyne, and anhydrite was identified with gehlenite, nepheline and hauyne being the dominant minerals, suggesting that the reaction between calcium and aluminum silicate occurred. As the ashing temperature further increased to 1100 °C, the remaining mineral phases in the ash were gehlenite, nepheline, and apinel with gehlenite being the dominant mineral. The formation of apinel at 1100 °C suggested that the interaction between periclase and alumina oxides occurred. The presence of Na- and Ca-bearing minerals such as nepheline, hauyne and gehlenite are responsible for the low fusion temperature of the ZL80IL20 ash.

Figure 4-11 Variations in the main mineral phases of the (a) ZL40AB60 ash, and (b) ZL20AB80 ash as a function of ashing temperature.
**ZL60IL40 and ZL50IL50 ashes:** Figure 4-12(b) and Figure 4-12(c) illustrate the variations in mineral phases in the ZL60IL40 and ZL50IL50 ash. It is clear that the mineral phases in the ZL60IL40 and ZL50IL50 ashes at 815 °C, with anhydrite, quartz, and hematite being dominant, were less complex than those in ZL80IL20 ash. In particular, Na-bearing minerals such as nepheline were not identified, suggesting that the ash became more refractory as the IL ratio increased. This is the reason why ash sintering temperature increased as the IL ratio increased. As ashing temperature increased, mullite and anorthite were identified in the ZL40IL60 and ZL50IL50 at 1000 °C and above. Moreover, the formation of nepheline and hauyne was inhibited in these ash samples. In addition, gehlenite was identified in the ZL40IL60 and ZL50IL50 at 1100 °C, but it was incorporated into other minerals or eutectics as the temperature further increased to 1200 °C. As ashing temperature increased to 1200 °C, the remaining minerals were spinel and anorthite in the ZL60IL40 ash, and were spinel, anorthite, and labradorite in the ZL50IL50 ash. The presence of mullite and the absence of nepheline and hauyne explain the increase in fusion temperatures as the IL ratio increased.

**ZL40IL60 and ZL20IL80 ashes:** Figure 4-13(a) and Figure 4-13(b) illustrate the variations in mineral phases in the ZL40IL60 and ZL20IL80 ash samples. It is clear that the mineral phases in these ash samples became less complex than those in the other ZL and IL blends. At 815 °C, anhydrite, quartz, and hematite were identified in the ash with anhydrite being the dominant mineral phase. As ashing temperature increased to 900 °C, the amount of anhydrite, quartz decreased, while hematite diminished. At 1000 °C and above, mullite and anorthite became the dominant mineral phases, while anhydrite, quartz and hematite disappeared.

Summarising the evidence discussed above, for ZL and IL blends, Na-bearing minerals such as nepheline and hauyne still existed in the ZL80IL20 ash, however they were absent as the IL addition ratio increased, leading to an increase in ash fusion temperatures as determined.

**AB and IL blends**

Table 4-8 summaries the mineral phases in the ash of AB and IL blends as a function of ashing temperature. It is obvious that the mineral phases in these ashes were similar to the ash samples from AB and IL, with quartz and mullite being dominant mineral phases.
Figure 4-12  Variations in the main mineral phases of the (a) ZL80IL20 ash, (b) ZL60IL40 ash, and (c) ZL50IL50 as a function of ashing temperature
Figure 4-13  Variations in the main mineral phases of the (a) ZL40IL60 ash, and (b) ZL20IL80 ash as a function of ashing temperature.
Table 4-6: Mineral phases identified in the ashes of ZL and AB blends at different ashing temperatures

<table>
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<tr>
<th>Samples</th>
<th>815 ºC</th>
<th>900 ºC</th>
<th>1000 ºC</th>
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<td>Anhydrite</td>
<td>Anhydrite</td>
<td>Anhydrite</td>
<td>Anhydrite</td>
</tr>
<tr>
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<td>Periclase</td>
<td>Periclase</td>
<td>Periclase</td>
<td>Periclase</td>
<td>Yeelimite</td>
</tr>
<tr>
<td>Yeelimite, Ca₄Al₆O₁₂SO₄</td>
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<td>Yeelimite</td>
<td>Yeelimite</td>
<td>Calcium silicate</td>
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</tr>
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<td>Lime</td>
<td>Cristobalite</td>
<td>Calcium Iron Oxide</td>
<td></td>
</tr>
<tr>
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<td>Calcium Silicate Hematite</td>
<td>Ca₂Fe₂O₃.₁₂</td>
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<td>Quartz</td>
<td>Akermanite-gehlenite,</td>
<td>Glass phase</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>Hauyne, Al₆Ca₂Na₆O₃₂S₂Si₆</td>
<td>Hauyne, Al₆Ca₂Na₆O₃₂S₂Si₆</td>
<td>Akermanite-gehlenite,</td>
<td>Wollastonite</td>
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<tr>
<td>Nepheline</td>
<td>Nepheline</td>
<td>Nepheline</td>
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<td>Hauyne, Al₆Ca₂Na₆O₃₂S₂Si₆</td>
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<td>Hauyne, Al₆Ca₂Na₆O₃₂S₂Si₆</td>
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<tr>
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<td>1000 °C</td>
<td>1100 °C</td>
<td>1200 °C</td>
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<td>(NaFeO$_2$)</td>
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<td>(Al$<em>{6}$Si$</em>{2}$O$_{13}$)</td>
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### Table 4-7: Mineral phases identified in the ashes of ZL and IL blends at different ashing temperatures

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<th>1100 °C</th>
<th>1200 °C</th>
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<td>Glass phase</td>
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<tr>
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<td>Na$<em>6$K$</em>{1.2}$Al$<em>{7.1}$Si$</em>{8.9}$O$_{32}$</td>
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<td>Ca$_2$Al$_2$SiO$_7$</td>
<td>Spinel MgAl$_2$O$_4$</td>
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<td>Slicate</td>
<td>(Al$_6$Si$<em>6$O$</em>{24}$)(SO$<em>4$)$</em>{1.52}$</td>
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<td>Quartz Anorthite</td>
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## Chapter 4 Characterisation of Ashes from Plasma Asher and Muffle Furnace

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<td>Quartz</td>
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<td>Anhydrite</td>
<td>Anatase</td>
<td>Quartz, Rutile</td>
<td>Al(Al₁.₂₇₂Si₀.₇₂₈O₄.₈₆₄)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anatase</td>
<td>Mullite</td>
<td>Anorthite</td>
<td>Cristobalite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mullite</td>
<td>Al₁.₈O₉.₆Si₂.₂</td>
<td>Anorthite</td>
<td>Cristobalite</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anatase</td>
<td></td>
<td></td>
<td>Al₁.₇₇Ca₀.₈₈O₈Si₂.₂₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rutile</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Anorthite</td>
</tr>
</tbody>
</table>
Table 4-8  Mineral phases identified in the ashes of AB and IL blends at different ashing temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>815 ºC</th>
<th>900 ºC</th>
<th>1000 ºC</th>
<th>1100 ºC</th>
<th>1200 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB20IL80</td>
<td>Quartz</td>
<td>Quartz, Mullite</td>
<td>Quartz, Mullite</td>
<td>Quartz Mullite</td>
<td>Mullite Quartz</td>
</tr>
<tr>
<td></td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Anatase Rutile</td>
<td>Cristobalite, Rutile</td>
</tr>
<tr>
<td>AB40IL60</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz, Mullite</td>
<td>Mullite, Quartz</td>
</tr>
<tr>
<td></td>
<td>Anatase</td>
<td>Mullite</td>
<td>Mullite</td>
<td>Hematite, Cristobalite</td>
<td>Cristobalite</td>
</tr>
<tr>
<td></td>
<td>Sodium Iron oxide</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Rutile</td>
<td>Rutil Albite</td>
</tr>
<tr>
<td>AB50IL50</td>
<td>Quartz, Anatase</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Mullite</td>
</tr>
<tr>
<td></td>
<td>Hematite</td>
<td>Mullite</td>
<td>Hematite</td>
<td>Mullite</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>Sodium Iron Oxide</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Hematite</td>
<td>Cristobalite</td>
</tr>
<tr>
<td></td>
<td>sodium Iron Oxide</td>
<td>Mullite</td>
<td>Mullite</td>
<td>Titanium Oxide</td>
<td>Hematite</td>
</tr>
<tr>
<td>AB60IL40</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Mullite, Quartz</td>
<td>Mullite, syn</td>
</tr>
<tr>
<td></td>
<td>Anatase</td>
<td>Hematite</td>
<td>Hematite</td>
<td>Cristobalite</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>Hematite</td>
<td>Anatase</td>
<td>Anatase</td>
<td>Hematite</td>
<td>Cristobalite</td>
</tr>
<tr>
<td></td>
<td>Sodium Iron Oxide</td>
<td>Mullite</td>
<td>Mullite</td>
<td>Titanium Oxide</td>
<td>Hematite</td>
</tr>
<tr>
<td>AB80IL20</td>
<td>Quartz Anatase</td>
<td>Quartz Hematite</td>
<td>Quartz</td>
<td>Quartz</td>
<td>Quartz Mullite</td>
</tr>
<tr>
<td></td>
<td>Hematite</td>
<td>Anatase</td>
<td>Hematite</td>
<td>Hematite</td>
<td>Cristobalite</td>
</tr>
<tr>
<td></td>
<td>Sodium Iron Oxide</td>
<td>Sodium Iron Oxide</td>
<td>Mullite</td>
<td>Mullite</td>
<td>Hematite</td>
</tr>
</tbody>
</table>
4.3 Effect of ashing temperature on the properties of the ZL ashes

The above characterisations on the chemistry, mineralogy, sintering temperature, fusion temperature, and mineral transformation of ash samples from coal and coal blends have provided sufficient data to understand the properties of the ash samples, permitting evaluation on the effect of coal blending on these properties and on ash deposition propensities. However, the above analysis also indicates that ashing temperature plays a significant role in the transformation of the mineral matter in coal. This brings the necessity of investigating the effect of ashing temperature on the properties of the ash. Among the three types of coal samples, Zhundong lignite are greatly affected due to its abundance in alkali and alkali earth contents in the ash (Zhang et al. 2015). Therefore, the effect of ashing temperature on the physicochemical properties of the Zhundong lignite ash samples was investigated. Ash samples were prepared at temperatures ranging from 550 °C to 1200 °C, and the ash yields, ash chemistry, ash mineralogy, ash morphology and ash sintering temperature were analysed.

4.3.1 Ash yield and chemical composition

Figure 4-14 shows the ash yields as a function of ashing temperature. It was apparent that the ash yield decreased with increasing ashing temperature. The ash yield was measured to be 3.7% at 550 °C, and decreased to 3.2% at 815 °C, and then dropped significantly to 2.1% at 1200 °C. This is because the increase in ashing temperature promoted the evaporation of Na, K and S and the decomposition of low temperature fluxing minerals as discussed below.

---

![Figure 4-14](Image) Ash yields as a function of ashing temperature
Chapter 4 Characterisation of Ashes from Plasma Asher and Muffle Furnace

The chemical compositions of the ashes at ashing temperature of 550 °C, 815 °C and 1200 °C were analysed using ICP-AES as shown in Table 4-9. It is clear that significant amounts of Ca, S, Na, and Mg were found in the ash at 550 °C. With increasing the ashing temperature up to 815 °C, the content of Na decreased, while the contents of Fe, K, S, and Ca increased. As the ashing temperature further increased to 1200 °C, the contents of Na, K, and S in ashes significantly decreased as they were easily vaporised at temperatures of 800 °C or above (Vuthaluru et al. 1998; Li et al. 2004; Xiao et al. 2011), while the contents of the other elements increased. The release of Na, K, and S also contributed to the decrease in ash yields as shown in Figure 4-14.

Table 4-9 Chemical composition of ash samples prepared at 550 °C, 815 °C and 1200 °C in muffle furnace in air

<table>
<thead>
<tr>
<th>Ashing temperature</th>
<th>Ash chemical compositions (10^2 ppm)</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>550 °C</td>
<td></td>
<td>847</td>
<td>393</td>
<td>435</td>
<td>335</td>
<td>2.10</td>
<td>992</td>
<td>11.9</td>
<td>2520</td>
<td>17.1</td>
<td>259</td>
</tr>
<tr>
<td>815 °C</td>
<td></td>
<td>388</td>
<td>451</td>
<td>405</td>
<td>284</td>
<td>0.82</td>
<td>1260</td>
<td>67.7</td>
<td>3040</td>
<td>13.3</td>
<td>298</td>
</tr>
<tr>
<td>1200 °C</td>
<td></td>
<td>53.6</td>
<td>833</td>
<td>837</td>
<td>594</td>
<td>1.86</td>
<td>251</td>
<td>12.4</td>
<td>3240</td>
<td>22.1</td>
<td>813</td>
</tr>
</tbody>
</table>

4.3.2 Ash mineralogy

Table 4-10 lists the mineral phases identified in ashes prepared at different ashing temperatures. It is clear that the ashing temperature significantly influenced the transformations of the mineral phases in the ashes. Typically, halite was identified at ashing temperature of 550 °C but disappeared at 700 °C and above. The Cl-bearing minerals existed in the ashes prepared at ashing temperatures of 550 °C and 700 °C but disappeared as the ashing temperature reached 815 °C and above. These indicated that Na and Cl had vaporised into gas phases at temperatures above 815 °C or incorporated into amorphous phases and glass phases. In addition, lime and periclase were formed since the ashing temperature reached 700 °C, which was believed to be caused by the decomposition of calcite and magnesite, respectively. It was also evident that yeelimite and calcium silicate were formed when the ashing temperature was equal to or higher than 815 °C. There were minor changes in the minerals phases of ashes as the ashing temperature increased from 815 °C to 1200 °C.
The characteristic peak intensity of each mineral phase is shown in Figure 4-15. As stated before, the characteristic peak intensity of each mineral phase represents its concentration in the ash. It is seen that anhydrite was abundant in the ash, and with increasing the ashing temperature, its content increased first and reached a peak at 1000 °C and decreased sharply afterwards. The content of calcite decreased sharply as the ashing temperature increased from 550 °C to 700 °C and continued to decrease but at a relatively slower rate as the ashing temperature further increased. Lime was identified in the ashes at the ashing temperature ranging from 700 °C to 1000 °C. The content of maganesite gradually decreased while the contents of periclase, yeelimite and calcium silicate increased with increasing the ashing temperature.

Table 4-10  Mineralogy of ashes at different temperatures in muffle furnace in air

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Mineral phases identified using XRD analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>Anhydrite, Calcite, Halite, Sodium calcium silicate, Calcium Phosphate Chloride Hydroxide, Magnesite</td>
</tr>
<tr>
<td>700</td>
<td>Anhydrite, Lime, Sodium calcium silicate, Calcite, Periclase, Calcium Hydroxide Chloride Silicate Sulfate, Magnesite</td>
</tr>
<tr>
<td>815</td>
<td>Anhydrite, Periclase, Yeelimite(Ca₄Al₆O₁₂SO₄), Lime, Cristobalite, Calcium silicate (Ca₂SiO₄), Magnesite</td>
</tr>
<tr>
<td>900</td>
<td>Anhydrite, Periclase, Yeelimite, Lime, Cristobalite, Calcium silicate, magnesite</td>
</tr>
<tr>
<td>1000</td>
<td>Anhydrite, Periclase, Yeelimite, Lime, Calcium silicate, Magnesite</td>
</tr>
<tr>
<td>1100</td>
<td>Anhydrite, Periclase, Yeelimite, Calcium silicate, Magnesium Iron Oxide</td>
</tr>
<tr>
<td>1200</td>
<td>Yeelimite, Perclase, anhydrite, Calcium silicate</td>
</tr>
</tbody>
</table>

The analysis of the ash mineralogy revealed that complex mineral reactions occurred during the ashing process. As the ashing temperature increased, the vaporisation of halite, the decomposition of calcite and maganesite, the formation of yeelimite and the decomposition of anhydrite progressively occurred. In particular, the vaporisation of halite and decomposition of calcite were mainly occurred prior to 1000 °C while the decomposition of anhydrite mainly occurred at temperatures higher than 1000 °C. These changes as a function of ashing temperature were also responsible for the decrease in the ash yield as shown in Figure 4-14.
Figure 4-15 The characteristic peak heights of major mineral phases as a function of ashing temperature
4.3.3 Ash morphology

The SEM observations on the morphology of the ashes are shown in Figure 4-16. It was revealed that the morphology of ash was dependent on ashing temperature. At ashing temperature 550 °C, discrete fine ash particles with size generally less than 20 μm were observed. As the ashing temperature increased, the ash particle started to sinter into agglomerates, and the sizes of the agglomerates increased. In fact, it was also found in the experiments that the strength of these agglomerates increased with increasing the ashing temperature as the agglomerates were gradually hard to be disrupted when external force was applied, indicating that the sintering degree of the agglomerates between ash particles increased. When the ashing temperature further increased to 1200 °C, the ash particles melted and fused into one bulk grain as shown in Figure 4-16(7). In the experiments, it was also found that it was very hard to remove the ash from the crucibles. The SEM observations indicated that increasing ashing temperature increased the formation of agglomerates as a result of ash sintering and melting of ash particles.

4.3.4 Ash sintering temperature

Figure 4-17 shows the effect of ashing temperature on the sintering temperatures of ash samples. It was obvious that sintering temperature of the ash increased as the ashing temperature increased, consistent with the ash chemistry and ash mineralogy analysis. At ashing temperature of 550 °C, the ash sintering temperature was the lowest due to the presence of significant amounts of AAEMs in the ash in the form of refluxing minerals such as halite. As the ashing temperature increased, the total contents of AAEMs in the ashes decreased through vaporisation and the contents of the refluxing minerals decreased after transformation into relatively refractory minerals. The ash sintering temperature therefore increased with increasing the ashing temperature.

It was also observed that the ash sintering temperature was higher than the ashing temperature at 550 °C, suggesting that the ash prepared at 550 °C was not sintered and the interactions between ash particles were less likely to occur. However, when the ashing temperature was higher than 700 °C, the ash sintering temperature was lower than the ashing temperature, indicating that the ash had already sintered in the muffle furnace during the ashing process. This is consistent with the ash morphology analysis as discussed above that sintered or fused ash particles were observed at high ashing temperatures while not observed at the ashing temperature of 550 °C.
Figure 4-16  SEM observations on the morphology of ash at various ashing temperatures: (1) 550 °C, (2) 700 °C, (3) 815 °C, (4) 900 °C, (5) 1000 °C, (6) 1100 °C, and (7) 1200 °C
Chapter 4 Characterisation of Ashes from Plasma Asher and Muffle Furnace

4.4 Conclusions

The effect of coal blending on the sintering, fusion and mineral transformation of coal ash was investigated. Coal blends between ZL and IL and between ZL and AB coals were prepared at ratios of 80:20, 60:40, 50:50, 40:60, and 20:80 respectively. Ash samples were prepared in muffle furnace in air at temperatures ranging from 815 °C to 1200 °C. The sintering temperatures and fusion temperatures of the ash samples prepared at 815 °C were determined, and the mineral phases in the ash subjecting to all ashing temperatures were identified.

Result shows that the ZL ash was rich in alkali and alkali earth contents in the forms of fluxing minerals such as anhydrite, calcium silicate and yeelimite, leading to relatively lower sintering and ash fusion temperatures. In contrast, the AB ash was rich in quartz and mullite, and the IL ash was abundant in mullite, quartz, and anorthite, leading to relatively higher sintering and fusion temperatures. As the ratio of AB or IL in the coal blends increased, the sintering temperature of the ash increased, suggesting that AB or IL coal would decrease the sintering tendency of the ZL ash at all blending ratio. The effect of AB or IL coal on fusion temperatures of the ZL ash samples, depending on the blending ratio, were not always increased as the ratio of AB or IL increased. For ZL and AB blends, a decrease in ash fusion temperatures of the blends was observed when the amount of AB in the blends was less than 50% due to the formation of Na-bearing minerals including nepheline and hauyne and the absence of refractory minerals such as
quartz and mullite. As the amount of AB in the blends further increased, the fusion temperatures of the ash increased due to the formation of mullite and the absence of fluxing minerals including nepheline and hauyne. For ZL and IL blends, hauyne and nepheline was identified in the blends at ZL80IL20, leading to a decrease in FT. As the IL ratio further increased, mullite was identified and the formation of nepheline was inhibited, and therefore increasing the ash fusion temperatures. In addition, the ash chemistry, ash mineralogy and mineral transformation, ash sintering temperature, and ash fusion temperatures of the IL and AB blends were also analysed. The results showed that the sintering temperature and ash fusion temperatures slightly increased as the AB ratio in the coal blends increased. However, the mineralogy of the ash and mineral transformation were similar to those in the AB and IL ashes, with quartz, mullite and cristobaline being dominant in the ash samples.

In addition, special attention was also paid to the effect of ashing temperature on the physicochemical properties of Zhundong lignite ash. It was found that the physicochemical properties of the Zhundong lignite ash were significantly dependent on the ashing temperature and the following conclusions can be drawn. Firstly, the ash yield decreased with increasing the ashing temperature, which was attributed to the vaporisation of Na, Cl, K, and S, and the decompositions of carbonates and sulphates such as calcite and anhydrite. Secondly, the minerals in the ashes transformed from low temperature refluxing minerals such as halite and calcite to relatively refractory minerals such as calcium silicate and yeelimite as the ashing temperature increased. Finally, the ash sintering temperature increased with increasing the ashing temperature. In addition, at the ashing temperature above 700 °C, the ash sintering temperatures were lower than the ashing temperatures, at which the ash has already sintered or even fused during ashing process.
Chapter 5 Effect of Coal Blending on Ash Fouling and Slagging during Combustion in Subcritical Boilers

Once an understanding of the thermal behaviour of the mineral matter in coal was established, the next step in this research was to study the characteristics of the ash deposits and investigate the effect of coal blending on the deposit behaviour and deposition mechanisms. This would allow investigation into the initiation, formation and growth of ash deposits on the heat transfer surfaces, and into the deposition characteristic, shedding lights upon the effect of coal blending and probe temperature on deposition mechanisms and deposit behaviour.

During the experimentation, a drop tube furnace was used to generate ash and an ash deposition probe was used for sample collection. Detailed description of the drop tube furnace and the ash deposition probe has been discussed in Figure 3-2. The temperatures of the probe top surface were controlled at 500 °C, 600 °C, 700 °C, and 750 °C, to simulate the ash deposition on superheaters in subcritical, supercritical and ultra-supercritical boilers, respectively. This chapter characterises the ash deposits formed on the probe at probe temperature of 500 °C, focusing on the effect of coal blending on ash deposition during combustion in subcritical boilers.

5.1 Ash mineralogy

5.1.1 Three base coals

Figure 5-1 shows the XRD patterns of the ZL, AB and IL ash deposits formed at probe temperature of 500 °C. It was found that the mineral phases in the ash deposits varied significantly with the types of coal.

ZL ash deposit: It is clear that anhydrite, quartz, nepheline, hematite, lime, periclase, and mullite were identified in the ZL deposit, with anhydrite being dominant. Among these minerals, anhydrite is a fluxing mineral that can act as an adhesive to enhance ash deposition during ash deposition (Bryers 1996; Kostakis 2011; Jing et al. 2013). Hematite and nepheline are also known to enhance ash deposition due to their low melting points (McLennan et al. 2000; Zhou et al. 2013; Zhou et al. 2014). Quartz and mullite are refractory minerals that can suppress the ash deposition. The high contents of fluxing minerals and low contents of refractory minerals found in the ash deposits
suggest severe sintering tendency and high deposition propensity of the Zhundong lignite during combustion (Li et al. 2016).

**AB ash deposit:** The mineral phases in the AB ash deposit at probe temperature of 500 °C were quartz, mullite and hematite with quartz and mullite being dominant mineral phases whereas hematite accounting for a minor fraction. The high contents of refractory minerals and low contents of fluxing minerals found in the ash deposit suggest low sintering tendency and low fouling and slagging propensity of the AB coal. The identification of quartz, mullite and hematite in the deposit was also consistent with the thermal behaviour of the mineral matter in the AB coal. As mentioned in the Chapter 4, quartz, mullite, and siderite were found in the AB coal. Quartz is one refractory mineral with high melting point and would retain its shape and phase during combustion (Raask 1985; Zhang 2013). Kaolinite would decompose and form mullite at temperatures higher than 1000°C (Raask 1985; Zhang 2013). Likewise, siderite would decompose and permitted the formation of hematite at high temperatures (Raask 1985; Zhang 2013).

**IL ash deposit:** As shown in Figure 5-1, the only mineral phase in the IL deposit at probe temperature of 500 °C was mullite. Mullite is one refractory mineral that can suppress the ash deposition (Bryers 1996). The abundance of mullite in the ash deposit indicates that the sintering tendency and deposition of the IL ash are low.

### 5.1.2 ZL and AB blends

**ZL80AB20 ash deposit:** As shown in Figure 5-2, the ZL80AB20 ash deposit, at probe temperature of 500 °C, was rich in quartz, anhydrite, lime, hematite, and mullite. Compared with the mineral phases in the ZL ash deposit at the same probe temperature, the peak intensity of quartz increased while the peak intensity of anhydrite decreased, indicating that more refractory minerals presented in the deposit due to the addition of AB. In addition, the fluxing mineral, nepheline, which was evident in ZL ash deposit, was not identified in ZL80AB20 ash deposit, indicating that the addition of AB at 20 wt% inhibited the formation of nepheline. Nepheline is a fluxing mineral which could stimulate ash sintering at low temperatures due to its low melting point (Li et al. 2016). The absence of nepheline in the deposit suggests that the ash deposition of Zhundong lignite could be mitigated with the addition of 20 wt% AB in the blend.
Figure 5-1  XRD patterns of the (a) ZL, (b) AB, and (c) IL ash deposits formed on the probe at probe temperature of 500 °C. Q – Quartz, Anh – Anhydrite, M – Mullite, L – Lime, N – Nepheline, H – Hematite, and P – Periclase
**ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 deposits:** It is clear that the mineral phases identified in these deposits at 500 °C as shown in Figure 5-2 were quartz, anhydrite, mullite and hematite where nepheline and hauyne were obviously absent, indicating that formation of Na-related fluxing minerals were inhibited. In addition, as the AB ratio in the blends increased, the peak intensities of the refractory minerals mainly quartz and mullite increased, while the peak intensity of anhydrite decreased and the other fluxing minerals disappeared, indicating that these deposits had more refractory minerals and became more refractory. The results also suggest that the ash sintering, fouling and slagging would be mitigated as the AB ratio in the blends increased.

**5.1.3 ZL and IL blends**

**ZL80IL20:** The mineral phases in the ash deposits of ZL and IL blends were shown in Figure 5-3. It was clear that quartz, anhydrite, lime, hematite, and mullite were identified in the ZL80IL20 ash deposit. The fluxing mineral, nepheline, which was evident in ZL ash deposit, was not identified in ZL80IL20 ash deposit, indicating that the addition of 20 wt% AB inhibited the formation of nepheline and suppress ash deposition. Moreover, compared with the mineral phases in the ZL ash deposit at the same probe temperature, the peak intensity of mullite increased while the peak intensity of anhydrite decreased, indicating that more refractory minerals presented in the deposit due to the addition of IL.

![XRD patterns of the ash deposits of ZL and AB blends formed on the probe at probe temperature of 500 °C. Q – Quartz, Anh – Anhydrite, M – Mullite, L – Lime, N – Nepheline, H – Hematite, and P – Periclase](image-url)
ZL60IL40, ZL50IL50, ZL40IL60, and ZL20IL80 deposits: It is clear that the mineral phases identified in these deposits at 500 °C (Figure 5-3) were mullite, anhydrite, and hematite where nepheline and hauyne were obviously absent, indicating that formation of Na-bearing fluxing minerals were inhibited. In addition, as the IL ratio in the blends increased, the peak intensity of the refractory mullite increased, while the peak intensity of anhydrite decreased and the other fluxing minerals disappeared, indicating that the deposits had more refractory minerals and became more refractory.

5.1.4 IL and AB blends

The mineral phases in the ash deposits of IL and AB blends were also identified as shown in Figure 5-4. It is obvious that the mineral phases in the IL75AB25, IL50AB50, and IL25AB75 ash deposits were quartz, mullite, and hematite. Similar to the mineral phases in the IL and AB ash deposits, quartz and mullite were still identified as the dominant mineral phases in these ash deposits, indicating that the blends also show low sintering tendency and deposition propensity. However, as the AB ratio in the blends increased, the peak intensity of quartz increased while that of mullite decreased, indicating that more quartz and less mullite presented in the deposits. In addition, hematite was still identified in the ash deposits but its content was low as indicated by its peak intensity. This indicates that hematite was not one dominant mineral phase in these deposits and its role in stimulating ash sintering may be suppressed by the refractory quartz and mullite minerals.

Figure 5-3  XRD patterns of the ash deposits of ZL and IL blends formed on the probe at probe temperature of 500 °C. Q – Quartz, Anh – Anhydrite, M – Mullite, L – Lime, N – Nepheline, H – Hematite, and P – Periclase
Figure 5-4  XRD patterns of the ash deposits of the IL and AB blends formed on the probe at probe temperature of 500 °C. M – Mullite, Q – Quartz, and H – Hematite

5.2 Ash morphology

5.2.1 Three base coal ashes

ZL ash deposit: Figures 5-5 presents typical SEM images of the ash deposit at 500 °C at various magnifications. The results of the EDS elemental analysis at selected spots of interest are also shown in the Figure 5-5. It was found that the ZL ash deposit was composed of particles of different sizes and shapes (Figure 5-5). The sizes of these particles or aggregates were estimated from the SEM images and widely ranged from sub-microns to 100 µm. Aggregates of fine particles were also observed in the deposit, e.g., particle F in Figure 5-5 (c), indicating that these fine particles were sticky and had sintered together during the deposition process (Luan et al. 2014). Furthermore, some of these fine sticky particles and their aggregates had adhered onto the surface of the coarse ash particles, e.g., particles G and H in Figure 5-5 (b), suggesting that the sintering between the fine particles and coarse particles also occurred. The shapes of the ash particles also varied. Smooth spherical ash particles, e.g., particles A and B in Figure 5-5 (b), suggest that these particles had experienced full molten during combustion. The presence of irregular particles, e.g., particles C and D in Figure 5-5 (b), means that these particles had high melting points and retained its original shapes during combustion.
Chapter 5 Effect of Coal Blending on Ash Deposition in Subcritical Boilers

Figure 5.5 Representative SEM images showing the morphological features of the ZL ash deposit at 500°C and the EDS results of elemental analysis at selected spots.

The EDS results as shown in Figure 5.5 (d) revealed the elemental composition of typical ash particles in the deposit at 500 °C. The spherical particle A in Figure 5.5 (b), according to EDS analysis (Area 1, Figure 5.5 (d)), was found to contain Fe and O, indicating the presence of iron oxides in the deposit. This iron oxide was identified as hematite from the XRD analysis shown in Figure 5.1. The spherical particle B in Figure 5.5 (b) was found to contain Na, Al, and Si (Area 2, Figure 5.5 (d)), indicating the presence of alkali aluminium silicates. Both hematite and alkali aluminium silicate have low melting points (Luan et al. 2014) and the particles containing these minerals melted during combustion and became spherical. The large irregular particle C in Figure 5.5 (b), which did not undergo melting during the combustion process, was mainly composed of Al and Si, with Na condensed on its surface (Area 3, Figure 5.5 (d)). The formation process of the irregular particle C was different from the spherical particle B (Hurley et al. 1992; Hurley et al. 1993; Vuthaluru et al. 1998), leading to similar ash chemistry but
a different shape. The large particle D was mainly composed of Si and O (Area 4, Figure 5-5 (d)), indicating the presence of quartz. These irregular particles had high melting points and retained their shapes during combustion. Fine ash particles, either individual or attached to coarse ash particles (e.g. particles E, F, G, and H in Figure 5-5 (b)), were mainly composed of Ca, S, and Mg (Area 5, Figure 5-5 (d)). The mineral forms of these particles were identified from the XRD analysis to be anhydrite, lime and periclase. These alkali earth-rich fine particles typically had relatively high viscosity and could act as glue and enhance ash sintering and deposition.

**AB ash deposit:** Figure 5-6 presents typical SEM images of the AB ash deposit at probe temperature of 500 °C and the EDS analysis at selected spots of interest. It is evident that, at probe temperature 500 °C, the AB ash deposit was mainly composed of discrete ash particles with sizes larger than 10 μm, where particle sintering was obviously absent. While there were some smooth spherical ash particles rich in iron oxide (area 1, Figure 5-6 (a)) and alkali aluminosilicate (area 2, Figure 5-6 (a)) presented, large irregular particles rich in silicate or aluminosilicate (particles C and D as examples) dominated the AB deposit, consistent with the XRD analysis that quartz and mullite were dominant in the ash deposit. These large irregular particles composed of silicate or aluminosilicate had high melting points and low viscosity, explaining the absence of particle sintering in the deposit.

**IL ash deposit:** Figures 5-7 presents typical SEM images of the IL ash deposit at 500 °C at various magnifications. It is evident that the IL ash deposit was mainly composed of coarse irregular ash particles where fine or spherical ash particles as well as particle sintering were absent. EDS analysis on the ash particles reveal that the ash particles were mainly rich in Si and Al, consistent with the XRD analysis that mullite was identified in the ash deposit. The abundance of mullite ash particles in the ash deposit suggests that the sintering, slagging and fouling propensities of the IL ash are low.

**5.2.2 ZL and AB blends**

Figure 5-8 represents the representative SEM images of the ash deposits of ZL and AB blends at 500 °C and the EDS results at selected spots of interest. It is obvious that the coal blending affected the sizes and chemistry of the ash deposits as well as the particle sintering.
Figure 5-6  Representative SEM images showing the morphological features of the AB ash deposit at 500 °C and the EDS results of elemental analysis at selected spots

**ZL80AB20:** It is obvious that the ZL80AB20 ash deposit at 500 °C composed of both coarse ash particles rich in Si and/or Al (areas 1 and 2, Figure 5-8 (a)), and fine ash particles rich in Ca, S, and Mg (areas 3 and 4, Figure 5-8 (a)). In addition, these fine ash particles seem to have stuck on the coarse ash particles as shown in Figure 5-8 (a), resulting in a decrease in the number of the discrete fine ash particles. This is confirmed by its particle size analysis as shown in Figure 5-9 that the particle size distribution curve of the ZL80AB20 ash shifted to larger ash particles compared to that the ZL ash. This is because the AB tended to form large particles rich in Si and Al, and the addition of AB into the ZL would increase the amount of large particles in the deposit. In addition, the large ash particles allowed for the capture of sodium vapour and fine alkali-earth ash particles (Figure 5-8 (a)), leading to a further decrease in the number of the discrete fine ash particles. This indicates that the addition of AB into the ZL coal provided large refractory ash particles in the ash deposit, allowing for the condensation of Na and the deposition of fine sticky ash particles, which means that the addition of
AB into the coal could suppress sintering between ash particles and mitigate ash deposition.

**Figure 5-7** Representative SEM images showing the morphological features of the IL ash deposit at 500 °C and the EDS results of elemental analysis at selected spots

**ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 deposits:** The morphological characteristics of the ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 ash deposits at probe temperature of 500 °C are also shown in Figure 5-8. The particle size distributions of the deposits are also given in Figure 5-9. It is observed that these deposits were mainly composed of large discrete ash particles where fine ash particles and particle sintering were obviously absent. As the AB ratio in the blends increased, the amount of large irregular particles in the deposits increased, while the amount of discrete fine particles (< 10 μm) decreased significantly. Compared to these of the ZL and ZL80AB20 ash deposits, fine ash particles and particle sintering were obviously absent in the ash deposits of these blends, indicating that the addition of AB into the coal suppressed sintering between ash particles and mitigate ash deposition. This mitigation effect also increased as the AB ratio in the coal blends increased.
Figure 5-8 Representative SEM images showing the morphological features of (a) ZL80AB20, (b) ZL60AB40, (c) ZL50AB50, (d) ZL40AB60, and (e) ZL20AB80 ash deposits at 500°C and the EDS results of elemental analysis at selected spots.
Figure 5-9  Size distribution curves of the ash deposits of the ZL and AB blends at probe temperature of 500 °C

5.2.3 ZL and IL blends

Figure 5-10 represents the representative SEM images of the ash deposits of ZL and IL blends at 500 °C and the EDS results at selected spots of interest. It is obvious that the coal blending affected the sizes and chemistry of the ash deposits as well as the particle sintering. For ZL80IL20 ash deposit as shown in Figure 5-10 (a), both irregular ash particles and spherical ash particles were observed in the ash deposit. EDS results show that the large ash particles, e.g., particles A and C, were rich in Si, Al, and/or Na, indicating the presence of aluminium silicate or sodium aluminium silicate. The fine spherical ash particles, e.g., particles B and D, were rich in Ca and S, indicating the presence of anhydrite ash particles. Compared with the ZL ash deposit, more large refractory ash particles and less fine ash particles presented in the ZL80IL20 ash deposit, indicating that the ash deposit had more aluminium silicate ash particles and became more refractory due to the addition of IL. Moreover, these fine ash particles have stuck on to the large irregular ash particles, indicating that the refractory ash particles had diluted the contact between fine particles and mitigate ash sintering and ash deposition.

As the IL ratio in the blends increased, more large refractory ash particles and less fine fluxing ash particles were observed in the ash deposits, as shown in figures 5-10 (b) ~ 5-10 (e). Moreover, due to the decrease in fine ash particles and increase in refractory ash particles, particle sintering was also absent as the IL ratio increased. This indicates that
sintering tendency and ash slagging and fouling propensities decreased as the IL ratio in the blends decreased.

Figure 5-10  Representative SEM images showing the morphological features of (a) ZL80IL20, (b) ZL60IL40, (c) ZL50IL50, (d) ZL40IL60, and (e) ZL20IL80 ash deposits at 500 °C and the EDS results of elemental analysis at selected spots.
5.2.4 IL and AB blends

The morphological features of the ash deposits of the IL and AB blends were also investigated as shown in Figure 5-11. It is obvious that these ash deposits were mainly composed of large irregular ash particles rich in Si, and/or Al, indicating the presence of refractory quartz and mullite ash particles in the deposits, consistent with the XRD analysis as shown in Figure 5-4. In addition, spherical ash particles (such as particle C in Figure 5-11 (a)) rich in Fe were also observed in the deposits, indicating the presence of hematite as identified in the XRD analysis. The abundance of refractory minerals and the absence of fluxing minerals indicate low sintering tendency and slagging tendency of the deposits.

5.3 Ash sintering temperatures

Sintering temperature of the ash deposits was determined to evaluate the effect of coal blending on ash deposition. Sintering is the bonding or welding between adjacent ash particles (Al-Otoom et al. 1999; Al-Otoom et al. 2000), which is one important mechanism for deposit development (Zbogar et al. 2009). Once the temperature of the outer layer of ash deposit reaches the sintering temperature, sintered or fused ash deposit will be formed (Zhang 2013). Therefore, sintering temperature has been regarded as a criterion for the evaluation of ash deposition propensity (Luan et al. 2014). A low sintering temperature indicates high sintering tendency and high deposition propensity, and vice versa.

Figure 5-12 shows the sintering temperatures of the ash deposits of the blends. It is clear that, for the ZL and AB blends, the sintering temperature of the deposit increased as the AB ratio in the coal blends increased. This indicates that the sintering tendency and ash deposition propensity of the blends were suppressed with increasing AB ratio in the coal blends. This is due to the differences in the chemistry and mineralogy of the ash deposits (Li et al. 2016). Firstly, as the AB ratio in the coal blends increased, the amount of silica and silicate increased while the amount of alkali and alkali earth decreased. This is reflected by the SEM-EDS analysis that more refractory ash particles rich in Si and Al were identified as the AB ratio increased. Secondly, the amounts of fluxing mineral phases, including anhydrite, lime, and nepheline that could stimulate ash sintering, decreased or even vanished as the AB ratio in the blends increased. Therefore, the sintering tendency decreased and the ash sintering temperature increased. However, the increase in ash sintering temperature was not linear with the AB ratio, showing a
significant increase when the AB ratio was lower than 50% and a slightly increase afterward. This is because the ash deposition is a selective process (Baxter 2000) and the chemistries of the deposits are speculated to be non-linear with the AB ratio, leading to a difference in elevating the ash sintering temperature as the AB ratio increased.

Figure 5-11  Representative SEM images showing the morphological features of (a) IL75AB25, (b) IL50AB50, and (c) IL25AB75 ash deposits at 500 °C and the EDS results of elemental analysis at selected spots
For ZL and IL blends, the sintering temperature of the ash deposit also increased as the IL ratio in the blends increased, indicating that the IL coal also suppress the ash deposition of ZL coal, consistent with the XRD and SEM-EDS analysis as discussed above. For IL and AB blends, the sintering temperatures of the ash deposits maintained at relatively high temperatures and varied in a small range, indicating that all these coal blends have low sintering, slagging and fouling propensity of the deposit.

Figure 5-12  Sintering temperatures of the (a) ZL and AB, (b) ZL and IL, (c) IL and AB ash deposits
5.4 Discussion

5.4.1 Ash deposition mechanisms

The mineralogy, morphology, and sintering characteristics of the deposits can also shed light upon the how deposition process during combustion of Zhundong lignite. Zhundong lignite ash is rich in Na, Ca and Mg. These elements in Zhundong lignite are mainly water soluble and ammonium acetate soluble (Li et al. 2015). When subjected to high flame temperatures, these elements were converted into calcium fume (CaO), periclase fume (MgO), and sodium vapour (Bryers 1996; Tomeczek et al. 2002; Yuan et al. 2015). Calcium fume may react with sulphur to form anhydrite, while sodium may react with sulphur generating sodium sulphate. These particles are mainly fine aerosol particles with sizes less than 10 μm. These fine particles also had low melting points and became sticky during combustion at 1400°C, leading to their adherence to other ash particles. The fine particles or vapour containing anhydrite, periclase, or sodium sulphate would uniformly deposit on the top and side surfaces by condensation, thermophoresis, and/or chemical reactions, and would initiate the ash deposition. Moreover, these fine particles rich in Ca, Mg, and S, and condensed Na-containing vapours could also act as glue and stimulate ash sintering in the later stages of ash deposition. Meanwhile, quartz and mullite were liberated from the organic matrix of Zhundong lignite during combustion. These silicates were able to interact with Na, Ca, Mg, and Al, resulting in the formation of nepheline or Ca/Mg/Al silicates (Vuthaluru et al. 1998). The absence of refractory minerals such as silicate and aluminosilicate also resulted in the low ash sintering temperature and high deposition propensity.

For the ash deposition of the AB and IL, the deposits were rich in refractory minerals such as silicate and aluminosilicate, and absent of fluxing ash minerals. The sintering temperatures of the ash deposits were also relatively high, indicating low fouling and slagging propensity of the ash particles.

5.4.2 Effect of coal blending

The mineralogy, morphology, and sintering characteristics of the deposits can also shed light upon the how the coal blending suppressed the ash deposition during combustion of ZL. When the AB and IL coal were added into ZL, the total amount of fine alkali-earth ash particles as well as the condensed vapours decreased while the refractory large irregular particles increased, as discussed above. In this case, the amount of main “culprits” in initiating ash deposition (Na, Ca, Mg, and S) decreased. Moreover, once
the refractory irregular large ash particles deposited on the probe, they diluted the contact between fine ash particles and provided more capability for the condensation of alkali as observed in Figures 5-8 and 5-10. For the coal blends, the refluxing mineral, nepheline, even disappeared in the deposits. Therefore, adding AB or IL coal into ZL increased ash sintering temperature and suppressed the fouling and slagging propensities of Zhundong lignite ash.

5.5 Conclusions

The mineralogy, morphology, and sintering temperature of the ash deposits formed on an air-cooled probe at probe temperatures of 500 °C during combustion of coal blends were systematically characterised. The ZL ash deposit was dominated by fluxing minerals including anhydrite, lime, hematite, and nepheline, with the presence of significant amount of fine particles (< 10 μm) and sintered particles, and had a relatively low sintering temperature, indicating high sintering tendency and severe fouling and slagging propensity. In contrast, the deposits from the bituminous coal and Indonesian lignite were dominated by refractory minerals including quartz and mullite with size larger than 10 μm, and had relatively high sintering temperatures, indicating low fouling and slagging propensity. The addition of AB or IL to ZL inhibited the formation of nepheline, increased the amount of quartz and mullite, and decreased the amount of fluxing minerals. Meanwhile, as the AB or IL ratio in the coal blends increased, the amount of fine particles in the deposits decreased and further diluted by the refractory ash particles, leading to mitigated particle sintering. As a criterion for evaluation of ash slagging and fouling, the sintering temperature of the deposit increased as the AB or IL ratio increased, indicating that the severe ash deposition of Zhundong lignite could be mitigated through coal blending.
Chapter 6 Effect of Coal Blending on Ash Fouling and Slagging during Combustion in Supercritical and ultra-Supercritical Boilers

The previous chapter has reported the characterisation of the ash deposits formed on the air-cooled probe at 500 °C during combustion of coal blends of Zhundong lignite and other coals, simulating ash deposition on superheaters in subcritical boilers. With the development of supercritical and ultra-supercritical boilers for higher thermal efficiencies, the steam temperature is increased which in turn elevates the surface temperature of the superheater tubes. The ash deposit behaviour and properties, and even the deposition mechanisms may differ as the temperature of the superheater surface increases. Therefore, this chapter reports the characterisation of the ash deposits formed on the probe at probe temperature of 500 °C, 600 °C, 700 °C, and 750 °C, focusing on the effect of probe temperature on ash deposition during combustion in supercritical and ultra-supercritical boilers.

6.1 Ash mineralogy
6.1.1 Three base coal ashes

**ZL ash deposits:** At probe temperature of 500 °C, the mineral phases in the ZL ash deposit were identified as anhydrite, quartz, lime, hematite, nepheline (Na_{6.65}Al_{6.24}Si_{9.76}O_{32}), periclase, and mullite, as shown in Figure 6-1(a). Among these minerals, fluxing minerals including anhydrite, nepheline, and hematite with high viscosity and low melting points were dominant while the refractory minerals such as quartz and mullite were deficient, indicating severe sintering tendency and high deposition propensity of the deposit (McLennan et al. 2000; Zhou et al. 2013; Zhou et al. 2014; Panagiotidis et al. 2015; Li et al. 2016). The mineral phases in the ZL ash deposit at 600 °C were the same with those in the ash deposit at 500 °C. However, as probe temperature further increased to 700 °C, hauyne, a low melting point mineral phase, was formed, indicating that mineral interactions and ash sintering had occurred in the ZL deposit at 700 °C. The detailed discussion on the mineral interactions as the probe temperature increased can be found in our previous publication (Li et al. 2016).

**AB ash deposits:** The mineral phases in the AB ash deposit (Figure 6-1(b)), at probe temperature of 500 °C, were identified as quartz, mullite and hematite, with refractory
minerals quartz and mullite being dominant. The high contents of refractory minerals and low contents of fluxing minerals suggest high melting point of the AB ash and low deposition propensity (Bryers 1996). As probe temperature increased from 500 °C to 750 °C, no significant variations in both the mineral phases and peak intensities were observed in the ash deposits, suggesting that the AB ash deposits were relatively refractory and resistant to the temperature change at the probe temperatures tested.

**IL ash deposits:** The mineral phases in the IL ash deposit (Figure 6-1(c)), at probe temperature of 500 °C, were identified as mullite, indicating the high melting point of the IL ash and low deposition propensity. As probe temperature increased from 500 °C to 750 °C, mullite was still identified in the deposits. In addition, cristobalite was identified in the ash deposit at 750 °C, indicating that mineral conversion or transformation had occurred in the ash. Even so, the abundance of mullite in the ash deposits suggests that the IL ash deposits were relatively refractory and resistant to the temperature change at probe temperature tested.

### 6.1.2 ZL and AB blends

**ZL80AB20 ash deposits:** As shown in Figure 6-2(a), the ZL80AB20 ash deposit, at probe temperature of 500 °C, were rich in quartz, anhydrite, lime, hematite, and mullite. However, as the probe temperature increased to 750 °C, while the mineral phases including quartz, anhydrite, lime, hematite, and mullite remained in the ash, nepheline was again appeared in the ZL80AB20 ash deposit (Figure 6-2), indicating that mineral interactions had occurred in the deposit. This also indicates that blending AB with ZL at the 20 wt% AB blending ratio could help in suppressing ash deposition problem at low probe temperature but such effect would diminish as the probe temperature was higher.

**ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 deposits:** From Figures 6-2(b) to 6-2(e), it is also clear that the mineral phases identified in these deposits at 500 °C were quartz, anhydrite, mullite and hematite where nepheline and hauyne were obviously absent, indicating that formation of Na-related fluxing minerals were inhibited. As the probe temperature increased from 500 °C to 750 °C, no significant variations in both the mineral phases and peak intensities in the deposits were observed, indicating that mineral interactions in the deposits were resistant to the change of the probe temperature tested.
Figure 6-1  XRD patterns of the ZL, AB and IL ash deposits formed on the probe at probe temperatures of 500 °C, 600 °C, 700 °C, and 750 °C. Q – Quartz, Anh – Anhydrite, M – Mullite, L – Lime, N – Nepheline, H – Hematite, Hau – hauyne, and C – Cristobalite.
6.1.3 ZL and IL blends

**ZL80IL20 and ZL60AB40 ash deposits:** The mineral phases in the ZL80IL20 ash deposits as a function of probe temperature are shown in Figure 6-3 (a). It is clear that at probe temperature of 500 °C, anhydrite, mullite, quartz, hematite, lime, were identified in the ZL80IL20 ash deposit. As probe temperature increased, while the previous mineral phases remained, nepheline was identified at 600 °C and above. Meanwhile, sodium aluminium silicate and yeelimite was identified at 700 °C and 750 °C, indicating that the mineral interactions had occurred in the deposits as probe temperature increased. The mineral phases in the ZL60IL40 ash deposit at probe temperature of 500 °C were anhydrite, mullite, and quartz. As probe temperature increased to 700 °C and above, while the previous mineral phases remained, sodium aluminium silicate and yeelimite were identified, indicating that the mineral interactions had occurred in the ZL80IL20.

**ZL50IL50, ZL40IL60, and ZL20IL80 ash deposits:** From Figure 6-3, it is also clear that the mineral phases identified in these deposits at 500°C were mullite and anhydrite where nepheline and hauyne were obviously absent, indicating that formation of Na-bearing fluxing minerals were inhibited. As the probe temperature increased from 500 °C to 750 °C, no significant variations in both the mineral phases and peak intensities in the deposits were observed, indicating that mineral interactions in the deposits were resistant to the change of the probe temperature tested. These results suggest that when the IL blending ratio was more than 50wt%, the ash deposition could be significantly suppressed. Such suppression effect varies little with the probe temperature.

6.1.4 IL and AB blends

Figure 6-4 shows the mineral phases in the ash deposits of IL and AB blends at different probe temperatures. It is evident that at probe temperature 500 °C, quartz and mullite were still the dominant mineral phases in these ash deposits. As the probe temperature increased from 500 °C to 750 °C, no significant variations in both the mineral phases and peak intensities in the IL50AB50 and IL25AB75 ash deposits were observed, indicating that mineral interactions in the deposits were resistant to the change of the probe temperature tested. However, cristobalite was identified in the IL25AB75 ash at 700 °C and 750 °C, indicating that mineral conversion or transformation had occurred in the IL75AB25 ash deposit as probe temperature increased to 700 °C and above.
Figure 6-2  XRD patterns of the (a) ZL80AB20, (b) ZL60AB40, (c) ZL50AB50, (d) ZL40AB60, and (e) ZL20AB80 ash deposits formed on the probe at probe temperatures of 500 °C, 600 °C, 700 °C, and 750 °C. Q – Quartz, Anh – Anhydrite, M – Mullite, L – Lime, N – Nepheline, and H – Hematite.
Figure 6-3  XRD patterns of the ash deposits of ZL and IL blends formed on the probe at probe temperatures of 500 °C, 600 °C, 700 °C, and 750 °C. 
Q – Quartz, Anh – Anhydrite, M – Mullite, N – Nepheline, S – Sodium aluminium silicate, Y – yeelimite and C – Cristobalite
Figure 6-4 XRD patterns of the (a) IL75AB25, (b) IL50AB50, and (c) IL25AB75 ash deposits formed on the probe at probe temperatures of 500 °C, 600 °C, 700 °C, and 750 °C. Q – Quartz, M – Mullite, and C – Cristobalite
6.2 Ash morphology

6.2.1 Three base coal ashes

**ZL ash deposit:** Figure 6-5 presents typical SEM images of the ZL ash deposits at various probe temperatures and the EDS results at selected spots of interest. The particle size distributions of the ash deposits are shown in Figure 6-6. At probe temperature 500 °C, as shown in Figure 4(a), smooth spherical ash particles, e.g., particles A and B, were observed, suggesting that these particles had experienced fully molten during combustion. The elemental compositions of particles A and B were mainly Fe and O (area 1, Figure 6-5 (a)), and Si, Al and Na (area 2, Figure 6-5 (a)), respectively, indicating the presence of iron oxides and alkali aluminosilicate. Meanwhile, coarse irregular particles, e.g., particles C and D, also existed in the deposit. EDS results show that particle C was mainly composed of Si and Al with Na condensed on its surface (area 3, Figure 6-5(a)), and particle D was composed of Si and O (area 4, Figure 6-5(a)). These irregular particles retained its shape during combustion due to their high melting points. Furthermore, fine particles less than 10 µm (e.g. particle E) and particle aggregates (e.g. particles F in Figure 6-5(a)) were also observed in the deposit, indicating that particle sintering had occurred. These fine particles, either individual or attached to coarse particles, were composed of Ca, Mg, and/or S (area 5, Figure 6-5 (a)).

In addition, according to the particle size distribution of the deposit as shown in Figure 5, the ZL ash deposit tends to have significant amount of fine ash particles (< 10 µm) in the deposit, consistent with the literature studies as reported in (Xu et al. 2013; Li et al. 2015). These alkali earth-rich fine ash particles had high viscosity and therefore would stimulate particle sintering and enhance ash deposition.

The morphology of the deposit at 600 °C shown in Figure 6-5(b) was similar to that at 500 °C, without significant differences being observed. However, as probe temperature further increased to 700 °C, the sizes of the particles in the deposit increased, as shown in Figure 6-6, indicating that severe sintering had occurred. As evidence, the areas 1, 2, 3, and 4 in Figure 6-5(c) were rich in Ca, S, Na, Si, and Al, confirming that anhydrite fine particles had melted and incorporated into these coarse particles at 700 °C, leading to the formation of hauyne and increased sizes of the ash particles.
Figure 6-5  Representative SEM images showing the morphological features of ZL ash deposits at the probe temperatures of 500 °C, 600 °C, 700 °C, and the EDS results of elemental analysis at selected spots
AB ash deposits: Figure 6-7 presents typical SEM images of the AB ash deposits at different probe temperatures and the EDS analysis at selected spots of interest. The particle sizes of the ash deposits are shown in Figure 6-8. It is evident that, at probe temperature 500 °C, the AB ash deposit was mainly composed of discrete ash particles with sizes larger than 10 μm, where particle sintering was obviously absent. While there were some smooth spherical ash particles rich in iron oxide (area 1, Figure 6-7(a)) and alkali aluminosilicate (area 2, Figure 6-7(a)) presented, large irregular particles rich in silicate or aluminosilicate (particles C and D as examples) dominated the AB deposit, consistent with the XRD analysis that quartz and mullite were dominant in the ash. These large irregular particles composed of silicate or aluminosilicate had high melting points and low viscosity, explaining the absence of particle sintering in the deposit. As probe temperature increased, the morphology and size distribution of the AB ash deposits remained the same from SEM-EDS and particle size analysis, confirming that the AB ash deposits were refractory and resistant to the change of the probe temperatures tested.
Figure 6-7  Representative SEM images showing the morphological features of AB ash deposits at the probe temperature of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C, and EDS results of elemental analysis at selected spots.
**IL ash deposits:** Figures 6-9 presents typical SEM images of the IL ash deposit at different probe temperatures. It is evident that the IL ash deposit at 500 °C was mainly composed of coarse irregular ash particles where fine or spherical ash particles as well as particle sintering were absent. EDS analysis on the ash particles reveal that the ash particles were mainly rich in Si and Al, consistent with the XRD analysis that mullite was identified in the ash deposit. The abundance of mullite ash particles in the ash deposit suggests that the sintering, slagging and fouling propensities of the IL ash are low. As probe temperature increased, no significant differences in the morphology of the IL ash deposits could be observed from SEM-EDS and particle size analysis, indicating that the IL ash deposits were refractory and resistant to the change of the probe temperatures tested.

**6.2.2 ZL and AB blends**

**ZL80AB20 ash deposits:** Typical SEM images of the ZL80AB20 ash deposits at various probe temperatures and the EDS results at selected spots of interest were shown in Figure 6-10. It is obvious that the deposit at 500 °C composed of both coarse ash particles rich in Si and/or Al (areas 1 and 2, Figure 6-10(a)), and fine ash particles rich in Ca, S, and Mg (areas 3 and 4, Figure 6-10(a)). In addition, these fine ash particles seem to have stuck on the coarse ash particles as shown in Figure 6-10, resulting in a decrease in the number of the discrete fine ash particles. This is confirmed by its particle size analysis as shown in Figure 6-11 that the particle size distribution curve of the...
ZL80AB20 ash shifted to larger ash particles compared to that the ZL ash. This is because the AB tended to form large particles rich in Si and Al, and the addition of AB into the ZL would increase the amount of large particles in the deposit. In addition, the large ash particles allowed for the capture of sodium vapour and fine alkali-earth ash particles (Figure 6-10 (a)), leading to a further decrease in the number of the discrete fine ash particles.

The probe temperature was found to have significant impact on the morphologies and particles sizes of the ZL80AB20 ash deposits. As probe temperature increased to 750 °C, larger agglomerates in the deposit were observed (Figure 6-10(d)) and the particle sizes of the deposits (Figure 6-11) increased. EDS analysis show that the large agglomerate in Figure 6-10(d) was mainly composed of coarse ash particles rich in Si and/or Al, and/or Na, with fine particles rich in Ca, S, and Mg sintered onto their surface. This indicates that the ash sintering in the ZL80AB20 ash deposit was facilitated as probe temperature increased to 750 °C. Ash sintering also promoted the mineral interactions, explaining the formation of nepheline in the deposit at 750 °C.

**ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 deposits:** Figures 6-12 to 6-15 shows the morphological characteristics of the ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 ash deposits at different probe temperatures. It is observed that these deposits were mainly composed of large discrete ash particles where fine ash particles and particle sintering were obviously absent. As the AB ratio in the blends increased, the amount of large irregular particles in the deposits increased, while the amount of discrete fine particles (< 10 µm) decreased significantly. Compared to these of the ZL and ZL80AB20 ash deposits, fine ash particles and particle sintering were obviously absent in the ash deposits of these blends. As probe temperature increased, the morphologies of the ZL60AB40, ZL50AB50, ZL40AB60, and ZL20AB80 ash deposits at the probe temperatures tested were quite similar to that at 500 °C, without significant difference being observed from SEM analysis. Meanwhile, no significant difference could be observed from particle size distribution curves of the deposits as probe temperature increased. This indicates that ash sintering and mineral interactions were not promoted as probe temperature increased, suggesting that these ash deposits were more refractory and resistant to the temperature change.
Figure 6-9  Representative SEM images showing the morphological features of IL ash deposits at the probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C, and EDS results of elemental analysis at selected spots
Figure 6-10 Representative SEM images showing the morphological features of ZL80AB20 ash deposits at the probe temperature of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C, and EDS results of elemental analysis at selected spots.
Figure 6-11  Particle size distribution of the ZL80AB20 deposit samples collected at probe temperature of 500 °C, 600 °C, 700 °C, and 750 °C

Figure 6-12  Representative SEM images showing the morphological features of ZL60AB40 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C
Figure 6-13  Representative SEM images showing the morphological features of ZL50AB50 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C

Figure 6-14  Representative SEM images showing the morphological features of ZL40AB60 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C
6.2.3 ZL and IL blends

Figures 6-16 to 6-20 represent the representative SEM images of the ash deposits of ZL and IL blends at different probe temperatures. It was found that probe temperature had affected the deposit morphology.

ZL80IL20 ash deposits: As shown in Figure 6-16 (a), both irregular ash particles rich in Si, Al, and/or Na and spherical ash particles rich in Ca and S, were observed in the ash deposit at 500 °C. Moreover, these fine ash particles have stuck on to the large irregular ash particles, indicating that particle sintering had occurred and the refractory ash particles had diluted the contact between fine particles and mitigate ash sintering and ash deposition. As probe temperature increased from 500 °C to 750 °C, particle sintering was still observed in the deposit. The ash sintering was also facilitated as new mineral phases such as nepheline had been formed (Figure 6-3).
ZL60IL40 ash deposits: As shown in Figure 6-17 (a), both irregular ash particles rich in Si, Al, and/or Na and spherical ash particles rich in Ca and S, were observed in the ash deposit at 500 °C. Moreover, even though the amount of fine fluxing ash particles were less than that in the ZL and ZL80IL20 ash deposits, the fine ash particles have stuck on to the large irregular ash particles, indicating that particle sintering had occurred. As probe temperature increased from 500 °C to 750 °C, particle sintering was still observed in the deposit. The ash sintering was also facilitated by the fact that mineral phases in the ash deposits had been changed as identified in the XRD analysis (Figure 6-3).

Figure 6-16  Representative SEM images showing the morphological features of ZL80IL20 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C

ZL50IL50, ZL40IL60, ZL20IL80 ash deposits: Figures 6-18 to 6-20 show the morphological characteristics of the ZL50IL50, ZL40IL60, and ZL20IL80 ash deposits at different probe temperatures. It is observed that these deposits were mainly composed
of large discrete ash particles where fine ash particles and particle sintering were obviously absent. As the IL ratio in the blends increased, the amount of large irregular particles in the deposits increased, while the amount of discrete fine particles (< 10 μm) decreased significantly. Compared to these of the ZL, ZL80IL20, and ZL60IL40 ash deposits, fine ash particles and particle sintering were obviously absent in the ash deposits of these blends. As probe temperature increased, the morphologies of the ZL50IL50, ZL40IL60, and ZL20IL80 ash deposits at the probe temperatures tested were quite similar to that at 500 °C, without significant difference being observed from SEM analysis. This indicates that ash sintering and mineral interactions were not promoted as probe temperature increased, suggesting that these ash deposits were more refractory and resistant to the temperature change.

Figure 6-17 Representative SEM images showing the morphological features of ZL60IL40 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C
Chapter 6 Effect of Coal Blending on Ash Deposition in SC/USC Boilers

Figure 6-18 Representative SEM images showing the morphological features of ZL50IL50 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C

Figure 6-19 Representative SEM images showing the morphological features of ZL40IL60 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C
6.2.4 IL and AB blends

The morphological features of the ash deposits of the IL and AB blends as a function of probe temperature are shown in Figures 6-21 to 6-23. These ash deposits were mainly composed of large irregular ash particles rich in Si, and/or Al, indicating the presence of refractory quartz and mullite ash particles in the deposits, consistent with the XRD analysis as shown in Figure 5-4. In addition, spherical ash particles rich in Fe were also observed in the deposits, indicating the presence of hematite as identified in the XRD analysis. The abundance of refractory minerals and the absence of fluxing minerals indicate low sintering tendency and slagging tendency of the deposits. As probe temperature increased, the morphologies of the IL75AB25, IL50AB50, and IL25AB75 ash deposits at the probe temperatures tested were quite similar to that at 500 °C, without significant difference being observed from SEM analysis. This indicates that these ash deposits were more refractory and resistant to the temperature change.
Figure 6-21  Representative SEM images showing the morphological features of IL75AB25 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C

Figure 6-22  Representative SEM images showing the morphological features of IL50AB50 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C
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Figure 6-23 Representative SEM images showing the morphological features of IL25AB75 ash deposits at probe temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 750 °C

6.3 Ash sintering temperatures

Figure 6-24 shows the sintering temperatures of the ash deposits of the blends at various probe temperatures. For ZL and AB blends, it is clear that, regardless of the probe temperature, the sintering temperature of the deposit increased as the AB ratio in the coal blends increased. This indicates that the sintering tendency and ash deposition propensity of the blends were suppressed with increasing AB ratio in the coal blends. For each blend or individual coal, the sintering temperatures of their ash deposits increased as the probe temperature increased, as shown in Figure 6-24. This is also attributed to the differences in chemistry and mineralogy of the ash deposits. Speculating to the reasons, the condensation of sodium vapour and the thermophoresis deposition of fine particles as the deposition mechanisms (Raask 1985; Baxter 2000; Wang et al. 2014) decreased as the probe temperature increased, which decreased the AAEM contents in the deposits and therefore increased the ash sintering temperature (Luan et al. 2014). In addition, the increase in ash sintering temperature as probe
temperature increased was also observed in the IL and ZL blends as well as the IL and AB blends, indicating that the increase in ash sintering temperature as a function of probe temperature is independent of coal types and blending ratios.

Figure 6-24  The sintering temperatures of the ash deposits at various blending ratios and probe temperatures
6.4 Discussion

6.4.1 Effect of probe temperature

Ash deposition is a selective dependent process that a suite of deposition mechanisms are at play. These mechanisms include the condensation of vaporised metal vapours, thermophoresis deposition of fine ash particles, inertia impaction of coarse ash particles and chemical reactions (Baxter 2000). Among these deposition mechanisms, condensation deposition, thermophoresis deposition and chemical reactions are dependent on the temperature of the heat transfer surface, i.e., the temperature of the probe (Baxter 2000; Zhang 2013). At relatively low probe temperature at 500 °C, some vaporised metals mainly sodium would be condensed on the probe surface, while fine ash particles would deposit on the surface through thermophoresis deposition caused by the temperature difference between the probe surface and the local gas environment. As probe temperature increased, condensation and thermophoresis deposition as the mechanisms would be decreased. In this case, the condensed species and fine ash particles would be decreased in the ash deposits at higher probe temperatures. As a result, sintering temperature of the ash deposit increased as the probe temperature increased.

Moreover, as probe temperature increased, the deposited ash particles on the probe surface would be subjected to higher probe temperature. If the sintering temperature of the ash deposit is low, the particles on the probe surface would become softened or even melted, leading to the sintering between ash particles in the deposit. This is observed in the ZL and ZL80AB ash deposits that ash sintering was facilitated as the probe temperature increased to 700 °C and above.

The probe temperature effect on the deposition process and deposit properties as discussed above shows competing effects that one decreases the condensation and thermophoresis deposition while the other one increases the sintering and sticking of ash particles (Wang et al. 2014). This weakens the differences between the ash deposits formed at different probe temperatures and increases the difficulty in discussing the probe temperature effect on deposition process and deposit characteristics.

6.5 Conclusions

The mineralogy, morphology, and sintering temperature of the ash deposits formed on an air-cooled probe at different probe temperatures during combustion of coal blends
were systematically characterised. At probe temperature of 500 °C, the ash deposit from Zhundong lignite was dominated by fluxing minerals including anhydrite, lime, hematite, and nepheline, with the presence of significant amount of fine particles (< 10 μm) and sintered particles, and had a relatively low sintering temperature. In contrast, the deposit from the bituminous coal and Indonesian lignite was dominated by refractory minerals including quartz and mullite with size larger than 10 μm, and had a relatively high sintering temperature. The addition of AB (or IL) to ZL inhibited the formation of nepheline, increased the amount of quartz and mullite, and decreased the amount of fluxing minerals. Meanwhile, as the AB (or IL) ratio ratio in the coal blends increased, the amount of fine particles in the deposit decreased and further diluted by the refractory ash particles, leading to mitigated particle sintering. As a criterion for evaluation of ash slagging and fouling, the sintering temperature of the deposit increased as the AB (or IL) ratio increased, indicating that the severe ash deposition of Zhundong lignite was mitigated through coal blending.

As probe temperature increased, mineral interactions and ash sintering on the probe were facilitated, leading to the formation of new mineral phases (hauyne and nepheline) and an increase in particle size in ZL, ZL80AB20, ZL80IL20, ZL60IL40 ash deposits. However, when the AB ratio in the coal blends was higher than 40% or the IL ratio higher than 50%, significant mineralogical and morphological changes were not observed even though the probe temperature increased, suggesting that these deposits were more refractory and more resistant to the temperature change.

In addition, as probe temperature increased, the sintering temperature of the ash deposit increased. This is attributed to the differences in chemistry and mineralogy of the ash deposits in which the condensation of sodium vapours and thermophoresis deposition of fine ash particles decreased as probe temperature increased, resulting in a decrease in AAEM contents in the deposits and therefore an increase in ash sintering temperature.
Chapter 7 Investigation into the Structural and Geochemistry Variations of the Ash Deposits for Mitigation of Zhundong Lignite Ash Deposition

The previous chapters have provided basic understandings on the ash deposition of three types of coal (Zhundong lignite, Indonesian lignite, and Australian bituminous) as well as the effect of coal blending and probe temperature on the ash deposition mechanisms and deposit characteristics. The results revealed that the severity ash deposition of Zhundong lignite is caused by the abundance of condensed sodium vapour and fine alkali-earth ash particles, and the absence of refractory silicate or aluminium silicate in the deposits. Blending the AB or IL coal into the ZL was found to be effective in increasing the sintering temperatures of the ash deposits, ameliorating the mineralogical and morphological features of the ash deposits, and therefore mitigating ash deposition of Zhundong lignite.

During sample collection process, however, the ash deposit was scraped from the probe top surface as one bulk ash deposit after each run. This sample collection method, which has been widely used in literature, however, is not able to investigate the structures of the ash deposits. As ash deposition is a time-dependent process, the chemical compositions and sizes of the ash particles may vary as the deposit grows. This brings the necessity of investigating the structural and chemical evolutions of the ash deposit as deposit accumulates. Moreover, while in developing ash deposition mitigation strategies, coal blending is not the only strategy to mitigate ash deposition of Zhundong lignite during combustion. Literature studies have also suggested that the use of additives, water washing could also be potential mitigation strategies for ash deposition of Zhundong lignite.

Therefore, this chapter focuses on the investigations of the physical structures and chemistry of the ash deposits, shedding lights upon the effect of coal blending, additives, and water washing on ash deposition and deposit structures of Zhundong lignite.

7.1 Structures of the Zhundong lignite ash deposits
As has been described in Chapter 3, the top surface of the probe was specially designed and was able to be removed from the probe body. During the experimentation, the Zhundong lignite was combusted in the drop tube furnace at nominal temperature of
1400°C. At probe temperature of 600°C, the experiments ran for 1, 4, 8, and 16 hours, respectively, to investigate the time effect on the structural evolutions of the ash deposits. Moreover, the temperature of the probe surface was also maintained at 550°C and 750°C for 4 hours to investigate the effect of probe temperature on the structural evolutions of the ash deposits. After each run, the deposit on the removable probe surface was embedded into cold resin, cross-sectioned, polished and coated prior to SEM-EDS analysis. The backscattered electron (BSE) images were obtained to acquire better image quality and deeper EDS analysis compared to secondary electron images.

7.1.1 Effect of time

Figure 7-1 shows the SEM-EDS results of the ash deposits at different deposition time at probe temperature 600 °C. At 1 hour as shown in Figure 7-1(a), the ash deposit, with a thickness of ca.100 µm, was mainly composed of fine particles with sizes being less than 25 µm, where large irregular ash particles were obviously absent. This is because the probe surface was initially clean and smooth, the large particles who retained their shapes during combustion due to high melting points would bounce back and leave the probe surface once they impact the probe surface (Troiano et al. 2014). The fine particles, however, would impact the surface and stick onto the surface or deposit on the surface by thermophoresis (Baxter 2000). As a result, the ash deposit consisted of fine particles with sizes being less than 25 µm.

As the deposition time increased, the thickness of the ash deposit increased, indicating that more ash particles were deposited on the probe. Moreover, in a layer at the bottom of the deposit close to the probe surface, the particles were still spherical with small sizes less than 25 µm, indicating that these fine particles initiated ash deposition of Zhundong lignite. The thickness of this initiation layer seems to be the same when the deposition time increased, implying that the initiation layer of the ash deposit was relatively stable as the ash particles deposited and accumulated on the probe. In the deposit above the layer of fine particles, both fine ash particle and large irregular particle were found, suggesting that the large irregular particles deposited afterwards on the probe after a layer of fine particles had formed.
Figure 7-1  Representative SEM-BSE images of the cross-sections of the ash deposits at (a) 1 h, (c) 4 h, (e) 8 h, and (g) 16 h, and the EDS analysis on ash particles at selected spots.
The elemental composition of the various ash particles in the deposits were also analysed and the results are presented in Figure 7-1 as well. It was found that the elemental composition varied with particles. Taking the ash deposit at the 4 h deposition time in Figure 7-1 (d) for instance, the fine particles (particles C and D in Figure 7-1 (d)) were rich in Ca, or Ca and S, indicating the presence of lime and anhydrite particles. The large irregular particles such as particles A and B in Figure 7-1 (d), were rich in Si, Al, and/or Na, indicating the presence of aluminium silicate and/or sodium aluminium silicate. The bright spherical particles, such as particle E, Figure 7-1 (d), were mainly rich in Fe and O, indicating the presence of iron oxides. More ash particles were analysed and the above analysis were applicable for the ash particles whose ash chemistry were not presented. These indicate that the initiation layer of the ash deposit was mainly composed of fine particles rich in Ca, Ca/S or Fe, while the outer layer of the deposit consisted of large irregular (sodium) aluminium silicates particle and the Ca-rich fine particles.

Furthermore, in order to investigate the variation in chemistry of the Ca-rich fine particles, EDS analysis on the fine particles in the deposit as a function of deposit thickness were performed. The S/Ca ratio (on a weight basis) of the fine particle was used to evaluate the sulphation degree of the particles. An average S/Ca ratio of these particles at deposit thickness of < 200 µm, 200 ~ 400 µm, and > 400 µm, respectively, was calculated and shown in Figure 7-2. It is clear that the S/Ca ratio of the fine particles in the 1 hour deposit within a thickness of 200 µm was 0.35. This value is much lower than the S/Ca ratio of anhydrite, 0.8, indicating that Ca in the deposit could be existed as anhydrite and other Ca-associated minerals such as lime or calcium aluminium silicate.

As deposition time increased, the S/Ca ratio of the Ca-rich fine particles at a thickness of 0 ~ 200 µm increased to 0.59 in the 4 hour deposit and to 0.87 in the 16 hour deposit, suggesting that the sulphation of calcium occurred as deposition time increased. This is because the retention time of these particles on the probe surface increased as deposition time increased, therefore increasing calcium sulphation and therefore the S/Ca ratio (Bryers 1996). At deposition time of 8 and 16 hours, the S/Ca ratio of the fine particles at deposit thickness of 0 ~ 200 µm were 0.83 and 0.87, suggesting that the Ca-rich fine particles were mainly existed as calcium sulphate.
Moreover, it is observed that the S/Ca ratio decreased in each deposit as the deposit thickness increased. This is because the retention time of these ash particles on the probe at higher distances was lower than those of the particles at the bottom, therefore decreasing the time for calcium sulphation (Bryers 1996; Anthony et al. 2001). As a result, the S/Ca ratio of the particles decreased as the deposit thickness increased.

Calcium sulphation is an exothermal reaction which would raise the particle temperature sufficiently to cause a sticky surface and increase particle capturing (Bryers 1996; Zhan et al. 2015). In addition, literature study also showed that calcium sulphation reaction is also a sintering process which would increase the strength of the deposit (Anthony et al. 2001). Therefore, the sulphation of calcium contributes, if not dominantly, significantly to the severity ash deposition problem on the superheaters in the utility boilers during combustion of Zhundong lignite.

7.1.2 Effect of probe temperature

Figure 7-3 shows the structures of the ash deposits formed at probe temperatures of 550 °C, 600 °C and 750 °C for 4 hours, respectively, and the EDS results on ash particles at selected spots. It is found that all the deposits had fine particles initially at the probe surface with a thickness of ca. 100 µm and the large irregular particles deposited above a layer of fine particles. Moreover, as probe temperature increased, the deposit thickness decreased from 400 µm, to 325 µm and to 225 µm. This is speculated
to the following reasons. Firstly, as probe temperature increased, the temperature gradient between the flue gas temperature and the probe surface decreased, therefore decreasing the thermophoresis deposition of fine particles (Baxter 2000; Zhang 2013). Secondly, as probe temperature increased, the particles with low melting points might became soft and promoted the sintering of ash particles, therefore decreasing the gaps between ash particles and densifying the deposit. As a result, the thickness of the deposit decreased as probe temperature increased.

DES results in Figure 7-3 revealed that these fine particles were generally rich in Ca, or Ca/S, and Fe, and the large irregular particles were rich in Al, Si, and/or Na. Again, the S/Ca ratio of the Ca-rich fine particles in the deposit as a function of deposit thickness was determined and is shown in Figure 7-4. At probe temperature of 550 °C, the S/Ca ratio of the Ca-rich fine particles at a thickness of 0 ~ 200 µm was measured to be 0.44, while the S/Ca value at 200~400 µm was still a little bit lower, 0.21, due to less retention time for calcium sulphation. As probe temperature increased, the S/Ca ratio of the fine particles at both the thickness of 0 ~ 200 µm and 200 ~ 400 µm increased, suggesting that the sulphation of calcium was promoted as probe temperature increased. This is because as probe temperature increased from 550 °C to 700 °C, the calcium sulphation was facilitated (Hurley et al. 1998; Anthony et al. 2001), therefore increasing the S/Ca ratio of the fine particles.

7.2 Effect of coal blending
7.2.1 ZL and AB blends
Figure 7-5 shows the structures of the ZL80AB20, ZL60AB40, ZL40AB60, and ZL20AB80 ash deposits formed on the probe at probe temperature of 600 °C for 4 hours. It is obvious that the thicknesses of the ash deposits vary significantly with the AB blending ratio. For the ZL80AB20 ash deposit, the thickness of the ash deposit was measured to be ~ 812 µm. This thickness was higher than the ZL ash deposit at 600 °C at the same experimentation time (~ 325 µm). This is due to the addition of AB into ZL as the AB coal had more ash contents, leading to more ash particles deposited on the probe surface. As the AB ratio increased to 40%, 60%, and 80%, the thicknesses of the ash deposits also increased to 1925, 2550, and 3100 µm, respectively. This indicates that more ash particles were deposited on the probe surface due to the addition of AB.
Figure 7-3  Representative SEM-BSE images of the cross-sections of the ash deposits at probe temperatures of (a) 550 °C, (b) 600 °C, and (c) 700 °C

It is also clear that the structures and chemistry of the ash deposits vary with the blending ratio. For the ZL ash deposit, the initiation layer of the ash deposit was mainly composed of fine particles rich in Ca, Ca/S or Fe, while the outer layer of the deposit consisted of both large irregular (sodium) aluminium silicates particle and the Ca-bearing fine particle. This trend still applies to the ZL80AB20 ash deposit as shown in
Figures 7-5(a) and 7-5(b). However, the ZL80AB20 ash deposit consisted of more refractory ash particles than the ZL ash deposit, and therefore diluting the deposition of fine ash particles. As the AB ratio increased to 40% and above, more refractory ash particles rich in Si, and/or Al, and/or Na were found in the ash deposits as shown in Figure 7-5. These large refractory ash particles existed as “skeleton” in the deposit, diluting the deposition of fine ash particles, making the deposits looser and less sticky than the ZL and ZL80AB20 ash deposit as indicated by their SEM images, and therefore mitigating ash deposition of Zhundong lignite.

![Graph showing variations in S/Ca ratio of deposited fine ash particles as a function of probe temperature and deposit thickness.](image)

**Figure 7-4** Variations in the S/Ca ratio of the deposited fine ash particles as a function of probe temperature and deposit thickness

### 7.2.2 ZL and IL blends

Figure 7-6 shows the structures of the ZL80IL20, ZL60IL40, ZL40IL60, and ZL20IL80 ash deposits formed on the probe at probe temperature of 600 °C for 4 hours. It is obvious that the thicknesses of the ash deposits vary significantly with the IL blending ratio. For the ZL80IL20 ash deposit, the thickness of the ash deposit was measured to be ~ 1050 µm. This thickness was higher than the ZL ash deposit at 600 °C at the same experimentation time (~ 325 µm). This is due to the addition of IL into ZL as the IL coal had more ash contents, leading to more ash particles deposited on the probe surface. As the IL ratio increased to 40%, 60%, and 80%, the thicknesses of the ash deposits also increased to 1250, 2000, and 2600 µm, respectively. This indicates that more ash particles were deposited on the probe surface due to the addition of IL.
Figure 7-5  Representative SEM-BSE images of the cross-sections of the (a) ZL80AB20, (b) ZL60AB40, (c) ZL40AB60, and (d) ZL20AB80 ash deposits at probe temperature of 600 °C
It is also clear that the structures and chemistry of the ash deposits vary with the blending ratio. For ZL ash deposit, the initiation layer of the ash deposit was mainly composed of fine particles rich in Ca, Ca/S or Fe, while the outer layer of the deposit consisted of large irregular (sodium) aluminium silicates particle and the Ca-rich fine particles. This trend still applies to the ZL80IL20 ash deposit as shown in Figures 7-6 (a) and 7-6 (b). However, the ZL80IL20 ash deposit consisted of more refractory ash particles than the ZL ash deposit, and therefore diluting the deposition of fine ash particles. As the IL ratio increased to 40% and above, more refractory ash particles rich in Si and Al were found in the ash deposits as shown in Figure 7-6. These large refractory ash particles existed as “skeleton” in the deposit, diluting the deposition of fine ash particles, making the deposits looser and less sticky than the ZL and ZL80IL20 ash deposit as indicated by their SEM images, and mitigating ash deposition of Zhundong lignite. Moreover, as shown in Figure 7-6, ash particles rich in Si, Al and Ca were identified in the deposits, indicating that the interactions between Ca and aluminium silicate had occurred. This also means that sulphation of Ca could be inhibited as part of Ca had been bonded with aluminium silicate. As the sulphation of calcium also contributes to ash sintering and ash deposition, the decrease in calcium sulphation also mitigate ash deposition of Zhundong lignite.

7.3 Effect of additives

7.3.1 Effect of kaolin

Figure 7-7 shows the structures of the ash deposits of the ZL coal with the addition of 0%, 1%, 2%, and 4% kaolin, respectively. It is obvious that these ash deposits were composed of fine ash particles whereas large ash particles were still absent. This is because the kaolin that being used during experimentation were fine powder with size less than 10 µm, which would not bring or form large ash particles during combustion. The thickness of the ash deposits also varied but at a relatively smaller range than the deposit thicknesses of the coal blends. EDS analysis on the ash particles shows that the addition of kaolin would not only form mullite ash particles as shown in Figure 7-7, the mullite ash particles would also bond Ca, resulting in the formation of calcium aluminium silicate in the deposits. This also means that sulphation of Ca could be inhibited as part of Ca had been bonded with aluminium silicate. As the sulphation of calcium contributes to ash sintering and ash deposition, the decrease in calcium sulphation also mitigate ash deposition of Zhundong lignite.
Figure 7-6  Representative SEM-BSE images of the cross-sections of the (a) ZL80IL20, (b) ZL60IL40, (c) ZL40IL60, and (d) ZL20IL80 ash deposits at probe temperature of 600 °C.
7.3.2 Effect of bauxite

Figure 7-8 shows the structures of the ash deposits of the ZL with the addition of 0%, 1%, 2%, and 4% bauxite, respectively. It is obvious that the thicknesses of the ash deposits increased as the amount of bauxite increased. Furthermore, as the amount of bauxite increased, more refractory ash particles were identified in the ash deposits. This indicates that the addition of bauxite would dilute the fine ash particles and mitigate ash deposition of Zhundong lignite.

7.4 Effect of water washing

Figure 7-9 shows the structures of the ash deposits of the ZL coal and water washed ZL coal. It is clear that both the ash deposits composed of fine ash particles and large ash particles, without significant difference being observed from SEM analysis. EDS analysis as shown in Figure 7-9 shows that the fine ash particles were rich in Ca, Mg, and S, whereas large ash particles were rich in Si, Al, and occasionally, Na.

Water washing was aimed to remove the water-soluble elements including Na in the ZL coal so that its severity ash deposition could be mitigated. However, the experimental results and analysis also suggest that the occurrence of Na in the deposits is difficult to be quantitatively identified and water washing may not sufficiently mitigate Zhundong lignite ash deposition. This is due to the following reasons. Firstly, Na content was not abundant in the deposit as shown in Figure 7-9, consistent with the literature study in (Zhou et al. 2014). Without water washing, Na was found in the form of sodium aluminium silicate. After water washing, sodium aluminium silicate ash particles were still identified in the deposit. Moreover, the Na in the forms of ultra-fine ash particles or aerosols in nanometres was not able to be detected. This increases the difficulty to quantitatively identify the amount of Na in the deposits. Secondly, as shown in Figure 7-9, abundant fine ash particles (< 10 µm) rich in Ca, Mg, and S were found to be initiated the Zhundong lignite ash deposition. After water washing, the fine ash particles rich in Ca, Mg, and S were still present and initiated ash deposition, indicating that the deposition of alkali-earth fine ash particles was still at play. This suggests that water washing alters the inorganic constituents in the lignite and can have a certain degree in mitigating ash deposition, but its effectiveness requires further and quantitative investigation.
Figure 7-7  Representative SEM-BSE images of the cross-sections of the (a) ZL, (b) ZL+1% kaolin, (c) ZL+2% kaolin, and (d) ZL+4% kaolin ash deposits at probe temperature of 600 °C
Figure 7-8  Representative SEM-BSE images of the cross-sections of the (a) ZL, (b) ZL+1% bauxite, (c) ZL+2% bauxite, and (d) ZL+4% bauxite ash deposits at probe temperature of 600 °C
7.5 Conclusions

The structure and geochemistry of the ash deposits formed on an air-cooled probe were analysed and the effect of time, probe temperature, coal blending, additives, and probe temperature was investigated. For ZL ash deposit, result shows that the 1 hour ash deposit was mainly composed of fine particles (< 25 µm) rich in Ca/S, Ca, or Fe, indicating that the low melting points anhydrite, lime, and hematite ash particles initiated ash deposition. As deposit accumulated, the large irregular particles rich in Al/Si, or Al/Si/Na were subsequently deposited on the probe. Moreover, the S/Ca ratio of the fine particles increased as the deposition time increased, suggesting that sulphation of calcium occurred on the probe. In addition, as probe temperature increased from 550 °C to 750 °C, the thickness of the deposits decreased. Meanwhile, the sulphation of calcium was promoted as probe temperature increased, resulting in an increase in the S/Ca ratio of the fine particles.
Coal blending has significant influence on deposit structure and chemistry. It was found that the thicknesses of the ash deposits increased as the AB or IL ratio in the blends increased. The refractory ash particles diluted the fine ash particles, making the deposit looser and less sticky than the ZL ash deposit, and therefore mitigating ash deposition of Zhundong lignite.

The use of additives also found to be change the structure and chemistry of the ash deposits. The addition of kaolin would introduce more mullite ash particles in the deposit and form calcium aluminium silicate ash particles, inhibiting the sulphation of calcium and therefore mitigating ash deposition. The use of bauxite showed a dilution effect and therefore mitigated ash deposition.

The structure and geochemistry of the ash deposits of Zhundong lignite and water washed Zhundong lignite did not show significant differences as analysis from the SEM-EDS analysis. This is because sodium aluminium silicate, as one existence form of Na, was still identified in the ash deposit.
Chapter 8 Integration, Evaluation and Implications of the Present Study

The experimental and analytical work embodied in this thesis study on the mineral matter in coal and coal ashes, the ash sintering behaviour and ash fusibility, ash deposits characteristics, and structural and chemical variations of the ash deposits has provided a solid understanding of the effect of coal blending and probe temperature on the deposit characteristics and deposition mechanisms during combustion of three coals including Zhundong lignite. Through a series of systematic investigations, the effect of coal blending as one mitigation strategy for ash deposition firing Zhundong lignite and other coals have been investigated and evaluated. Likewise, the effect of probe temperature in simulating ash deposition on superheaters in subcritical, supercritical and ultra-supercritical boilers has also been studied. The detailed characterisation of the mineral matter in coal and ash deposits provides foundation to evaluate ash deposition behaviour during combustion.

This chapter integrates and evaluates the results and findings from this study, and provides implications of the present study in practical application and scientific understandings of ash deposition.

8.1 Integration and comparison of the experimental findings

8.1.1 The mineralogy of the ashes from muffle furnace and drop tube furnace

The previous chapters have mainly discussed two types of ash samples with one produced from muffle furnace and the other from drop tube furnace. The properties of these ash samples from the same coal sample varied with furnace temperature and probe temperature, allowing the ash samples from muffle furnace and ash deposits from drop tube furnace to be compared and evaluated.

Zhundong lignite ashes

Zhundong lignite is a type of lignite with high alkali and alkali earth contents but low silica, aluminium and aluminosilicate in the ash. Table 8-1 summaries the mineral phases that identified in the Zhundong lignite ash samples subjecting to different furnace temperatures and probe temperatures as presented in Chapters 4 and 5 (Table 4-7 and Figure 6-1(a)). XRD analysis on the lignite sample indicates that the mineral matter in coal mainly exists as organically-bound elements or included-minerals as no
X-ray diffraction peaks were identified (Chapter 4). The low temperature ash sample from plasma asher at 150 °C supported the abundance of fluxing minerals such as calcium sulphate, calcium carbonate, and sodium nitrate. Subjecting to different combustion temperatures in muffle furnace, the properties of the ash varied due to complex chemical and physical changes in the ash. The ash sample at ashing temperature of 550 °C was rich in Ca, S, Na, and Fe (Table 4-9) in the forms of either fluxing minerals such as anhydrite, calcite, halite, and sodium calcium silicate or amorphous phases (Table 4-10), leading to low sintering temperature and thus high sintering tendency of the ash (Chapter 4). As ashing temperature gradually increased to 1200 °C, the vaporisation of Na, Cl, K, and S, and the decompositions of carbonates and sulphates including calcite and anhydrite occurred in the ash (Table 4-9), leading to a decrease in the overall ash yield as a function of ash temperature (Figure 4-14). Moreover, the minerals in the ashes transformed from low temperature refluxing minerals such as halite and calcite to relatively refractory minerals such as calcium silicate and yeelimite as the ashing temperature increased. However, the dominant mineral phases in the ash deposits formed on the probe were identified as anhydrite, quartz, mullite, nepheline, hematite and lime, which are different from those identified in the ash samples that prepared in muffle furnace. In particular, mullite, which is a high melting point mineral, was found in the deposits while was absent in the ash from muffle furnace. Meanwhile, low melting-point nepheline and/or hauyne were present on the probe while were not identified in the ash samples from muffle furnaces. The difference in ash mineralogy was attributed to the difference in the fates of mineral matter during combustion in muffle furnace and drop tube furnace, which will be discussed in the next section.

**Australian bituminous ashes**

Table 8-2 summaries the mineral phases in the ash samples in muffle furnace (Table 4-6) and ash deposit samples in drop tube furnace (Figure 6-1(b)) during combustion of the Australian bituminous. It is obvious that the mineral phases in the Australian bituminous coal were identified as quartz, kaolinite, silicon oxide, siderite with quartz and kaolinite being dominant, indicating the presence of abundant silica or silicates in coal.
Table 8-1  Mineral phases in the ZL ashes prepared in muffle furnace at different temperatures and in ZL ash deposits formed on the probe in drop tube furnace

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>150°C_ Plasma asher</td>
<td>Calcium sulphate hydrate, Quartz, Calcium carbonate, Sodium nitrate, anhydrite, Magnesium Silicate Hydroxide, Ammonium Aluminum Phosphate Hydrate</td>
</tr>
<tr>
<td>550 °C_ Muffle furnace</td>
<td>Anhydrite, Calcite, Halite, Sodium calcium silicate, Calcium Phosphate Chloride Hydroxide, Magnesite</td>
</tr>
<tr>
<td>700 °C_ Muffle furnace</td>
<td>Anhydrite, Lime, Sodium calcium silicate, Calcite, Periclase, Calcium Hydroxide Chloride Silicate Sulfate, Magnesite</td>
</tr>
<tr>
<td>815 °C_ Muffle furnace</td>
<td>Anhydrite, Periclase, Yeelimite(Ca₄Al₆O₁₂SO₄), Lime, Cristobalite, Calcium silicate (Ca₂SiO₄), Magnesite</td>
</tr>
<tr>
<td>900 °C_ Muffle furnace</td>
<td>Anhydrite, Periclase, Yeelimite, Lime, Cristobalite, Calcium silicate, magnesite</td>
</tr>
<tr>
<td>1000 °C_ Muffle furnace</td>
<td>Anhydrite, Periclase, Yeelimite, Lime, Calcium silicate, Magnesite</td>
</tr>
<tr>
<td>1100 °C_ Muffle furnace</td>
<td>Anhydrite, Perclase, Yeelimite, Calcium silicate, Magnesium Iron Oxide</td>
</tr>
<tr>
<td>1200 °C_ Muffle furnace</td>
<td>Yeelimite, Perclase, anhydrite, Calcium silicate</td>
</tr>
<tr>
<td>1400 °C_ DTF_Probe at 500 °C</td>
<td>Anhydrite, quartz, nepheline, hematite, lime, periclase, and mullite</td>
</tr>
<tr>
<td>1400 °C_ DTF_Probe at 600 °C</td>
<td>Anhydrite, quartz, nepheline, hematite, lime, periclase, and mullite</td>
</tr>
<tr>
<td>1400 °C_ DTF_Probe at 700 °C</td>
<td>Anhydrite, quartz, nepheline, hauyne, hematite, lime, periclase, and mullite</td>
</tr>
</tbody>
</table>

The mineral phases in the muffle furnace ash at 815 °C were quartz, titanium oxide, sodium iron oxide and hematite with quartz being dominant in the ash. As ashing temperature increased, these mineral phases at 815 °C decreased whereas mullite was formed at 1100 °C and its content further increased as ashing temperature increased to 1200 °C. The presence of refractory minerals such as mullite and quartz with high...
melting points explains the high fusion temperatures of the AB coal ash (Raask 1985; Baxter 2000; Bryant et al. 2000; van Dyk 2006; Song et al. 2009; Xu et al. 2015).

In addition, the mineral phases in the deposits on the probe in drop tube furnace were identified as quartz, mullite and hematite with quartz and mullite being dominant minerals. The abundance of refractory minerals in the deposits and the absence of fluxing minerals also indicate low fouling and slagging propensity of the deposit.

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C_ Plasma asher</td>
<td>Quartz, Kaolinite, Silicon Oxide, Siderite,</td>
</tr>
<tr>
<td></td>
<td>Magnesium aluminium carbon hydrate</td>
</tr>
<tr>
<td>815 °C_ Muffle furnace</td>
<td>Quartz, hematite, titanium oxide, sodium iron oxide</td>
</tr>
<tr>
<td>900 °C_ Muffle furnace</td>
<td>Quartz, hematite, sodium iron oxide</td>
</tr>
<tr>
<td>1000 °C_ Muffle furnace</td>
<td>Quartz, hematite, titanium oxide, rutile</td>
</tr>
<tr>
<td>1100 °C_ Muffle furnace</td>
<td>Quartz, mullite, rutile</td>
</tr>
<tr>
<td>1200 °C_ Muffle furnace</td>
<td>Quartz, mullite, rutile</td>
</tr>
<tr>
<td>1400 °C_ DTF _Probe at 500 °C</td>
<td>Quartz, mullite, hematite</td>
</tr>
<tr>
<td>1400 °C_ DTF _Probe at 600 °C</td>
<td>Quartz, mullite, hematite</td>
</tr>
<tr>
<td>1400 °C_ DTF _ Probe at 700 °C</td>
<td>Quartz, mullite, hematite</td>
</tr>
<tr>
<td>1400 °C_ DTF _ Probe at 750 °C</td>
<td>Quartz, mullite, hematite</td>
</tr>
</tbody>
</table>

**Indonesian lignite ashes**

Table 8-3 summaries the mineral phases in the Indonesian lignite ashes prepared in muffle furnace (Table 4-7) and the ash deposits on the probe (Figure 6-1(c)). It is apparent that the Indonesian lignite rich in kaolinite, dolomite and silicon oxide (or) quartz. The IL ash prepared at 815 °C in the muffle furnace were dominated by acidic oxides including SiO₂ and Al₂O₃, suggesting the abundance of silica, silicates, or aluminosilicate in the ash. As the ashing temperature increased to 1200 °C, the mineral phases in the ash transformed from quartz and anhydrite to mullite, cristobalite, and anorthite. The presence of refractory minerals such as mulllite, quartz, and cristobalite caused the high fusion temperatures of the IL ash.
While identifying the mineral phases in the ash deposits on the probe during combustion of Indonesian lignite, it was found that the IL ash deposits on the probe were mainly consisted of large irregular ash particles with mullite being identified in the deposit, indicating that the propensity of the ash to foul and slag is relatively low.

**ZL and AB blends**

The investigation into the mineralogy of ash blends also allowed to examine the difference in the muffle furnace ashes (Table 4-6) and the ash deposits (6-2(b)). For the ash samples prepared in muffle furnace at 815 °C, quartz, hematite, and anhydrite were identified in the ashes of the blends. Moreover, Na-bearing minerals such as nepheline and hauyne were identified in the ZL80AB20, ZL60AB40, and ZL50AB50 blends ash as a result of mineral interaction. These Na-bearing minerals have even lower melting points than the Ca-bearing minerals, and therefore decreased the ash fusion temperatures including ST and FT. In other words, the AB ash, promoted the melting of Zhundong lignite ash when the ratio of AB in the blends was less than 50%. As the amount of AB in the blends further increased, mullite was formed in the ash while the formation of Na-bearing fluxing minerals was inhibited.

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C_ Plasma asher</td>
<td>Kaolinite, Quartz, Magnesium aluminium carbon hydrate</td>
</tr>
<tr>
<td>815 °C_ Muffle furnace</td>
<td>Quartz, anhydrite, anatase</td>
</tr>
<tr>
<td>900 °C_ Muffle furnace</td>
<td>Quartz, anatase, mullite</td>
</tr>
<tr>
<td>1000 °C_ Muffle furnace</td>
<td>Quartz, mullite, anatase</td>
</tr>
<tr>
<td>1100 °C_ Muffle furnace</td>
<td>Mullite, quartz, rutile, anorthite, cristobalite</td>
</tr>
<tr>
<td>1200 °C_ Muffle furnace</td>
<td>Mullite, cristobalite, rutile, anorthite</td>
</tr>
<tr>
<td>1400 °C_ DTF _Probe at 500 °C</td>
<td>Mullite</td>
</tr>
<tr>
<td>1400 °C_ DTF _Probe at 600 °C</td>
<td>Mullite</td>
</tr>
<tr>
<td>1400 °C_ DTF _Probe at 700 °C</td>
<td>Mullite</td>
</tr>
<tr>
<td>1400 °C_ DTF _Probe at 750 °C</td>
<td>Mullite, Cristobalite</td>
</tr>
</tbody>
</table>
In terms the mineral phases in the deposits of the blends, quartz, mullite, anhydrite, and hematite were mainly identified in the deposits. The addition of Australian bituminous to Zhundong lignite inhibited the formation of nepheline, increased the amount of quartz and mullite, decreased the amount of fluxing minerals, and therefore mitigated ash deposition.

**ZL and IL blends**

The mineral phases in muffle furnace ashes (Table 4-7) and ash deposits (Figure 6-3) of the blends of the Zhundong lignite and Indonesian lignite were also varied. For the muffle furnace ashes at 815 °C, Na-bearing minerals such as nepheline and hauyne still existed in the ZL80IL20 ash. As the Indonesian lignite addition ratio in the coal blends increased, more quartz was identified in the ash samples and formation of nepheline and hauyne was inhibited. For the ash deposits formed on the probe, refractory mineral mullite was identified in all ash deposits of the blends, which was not identified in the ashes at 815 °C in muffle furnace. In addition, sodium aluminium silicate and nepheline were identified in the ZL80IL20 ash deposit. As the Indonesian lignite addition ratio further increased, the formation of sodium aluminium silicate and nepheline was inhibited, indicating that the ash deposits were more refractory as Indonesian lignite was added to Zhundong lignite.

**AB and IL blends**

The mineral phases in the ashes of the blends of Australian bituminous and Indonesian lignite during combustion in muffle furnace and drop tube furnace were also compared (Table 4-8 and Figure 6-4). It was clear that the ash samples and the ash deposits samples of AB and IL blends were all rich in quartz and mullite with the absence of fluxing mineral phases. These indicate that these coal ash and ash deposit samples have low slagging and fouling propensities.

**8.1.2 Sintering temperature of the ash samples and the ash deposits**

The sintering temperatures of the ash samples from muffle furnace and the ash deposits from DTF at different probe temperatures were also compared as shown in Figure 8-1. It is obvious that the sintering temperatures of the ash samples and ash deposits increased as the AB ratio in the ZL and AB blends increased. Similar trend was also applied for the sintering temperatures of the ZL and IL blends as the ZL ratio in the blends increased. This confirms that sintering temperature could be used as one criterion
to evaluate the fouling propensity of the ash deposits, and supports the conclusion that the addition of AB or IL into ZL coal could be one mitigation strategy for ash deposition of Zhundong lignite.

In addition, it is worth noting that the sintering temperatures of the ZL ash deposits were lower than that of the ZL ash prepared in muffle furnace at 815 °C. This is attributed to the difference in the chemistry and mineralogy of the ashes due to their different formation processes. During ashing in muffle furnace at 815 °C, a significant amount of Na had been vaporised and escaped from the ash sample, resulting in a decrease in the contents of alkali or even alkali earth contents. However, ash formation on the probe at temperatures between 500 °C and 750 °C allowed condensations of the vaporised alkali and alkali earth species on the probe, increasing the low melting-point mineral phases and decreasing ash sintering temperature.

Figure 8-1 Sintering temperatures of the ash samples from muffle furnace at 815 °C and the ash deposits prepared at probe temperatures of 500 °C, 600 °C, 700 °C, and 750 °C
Moreover, it is also noted that the sintering temperatures of the AB ash deposits were higher than that of the AB ash prepared in muffle furnace at 815 °C. This is again attributed to the difference in the chemistry and mineralogy of the ashes due to their different formation processes. In particular, significant amount of mullite ash particles were identified in the deposits, which would increase the sintering temperature of the ash deposit. In contrast, the mineral phases in the muffle furnace ash were mainly identified as quartz and hematite with the absence of high melting-point mullite, and therefore had relatively low ash sintering temperature.

8.1.3 Ash deposition mechanisms

8.1.3.1 Zhundong lignite ash deposition

The ash deposition and deposits characteristics during the combustion of Zhundong lignite in a drop tube furnace at 1400 °C were studied (Chapter 5). Based on the experimental results, a schematic representation of the key mechanisms showing the role of the main mineral phases and processes of ash deposition during the combustion of Zhundong lignite is shown in Figure 8-2. As shown in Table 3-1, Zhundong lignite ash is rich in Na, Ca and Mg. These elements in Zhundong lignite are mainly water soluble and ammonium acetate soluble (Li et al. 2015). When subjected to high flame temperatures, these elements were converted into calcium fume (CaO), periclase fume (MgO), and sodium vapour (Bryers 1996; Tomeczek et al. 2002; Yuan et al. 2015). Calcium fume may react with sulphur to form anhydrite, while sodium may react with sulphur generating sodium sulphate. These particles are mainly fine aerosol particles with sizes less than 10 μm. These fine particles also had low melting points and became sticky during combustion at 1400 °C, leading to their adherence to other ash particles. The fine particles or vapour containing anhydrite, periclase, or sodium sulphate would uniformly deposit on the probe surface by condensation, thermophoresis, and/or chemical reactions, and would initiate the ash deposition. Meanwhile, quartz and mullite were liberated from the organic matrix of Zhundong lignite during combustion. These silicates were able to interact with Na, Ca, Mg, and Al, resulting in the formation of nepheline or Ca/Mg/Al silicates (Vuthaluru et al. 1998). As a result, the ZL ash deposit on the air-cooled probe at probe temperature of 500 °C was dominated by fluxing minerals including anhydrite, lime, hematite, and nepheline, with the presence of significant amount of fine particles (< 10 μm) and sintered particles, and had a relatively low sintering temperature.
The mechanisms of ash deposition during combustion of Zhundong lignite were also studied through the analysis of the deposit structures in Chapter 7. It was found that the ash deposit on the probe was initiated by fine ash particles rich in Ca, S, and Na, with large refractory minerals (quartz, mullite) deposited on the top of these fine ash particles afterwards. The fine ash particles might deposit on the probe surface through condensation or thermophoresis mechanism while the large refractory ash particles were due to inertia impaction. Meanwhile, chemical reactions between Ca in the deposit and the sulphate oxide in the gas phase occurred was confirmed by the evidence that the S/Ca ratio of the inner layer deposit was higher than the outer layer deposit. In addition, Na, as a dominant ash deposition initiator, either condensed on the surface of the probe as sodium sulphate or was captured by aluminosilicate and formed sodium aluminosilicate, nepheline or hauyne in the deposit.

Figure 8-2 A schematic representation of the deposition mechanisms and processes of the main mineral phases during the combustion of Zhundong lignite

These systematic studies on the ash properties and deposition behaviour of Zhundong lignite revealed that Zhundong lignite has high ash sintering, fouling and slagging propensities due to its high alkali and alkali earth contents as well as low contents of refractory minerals. The fine fluxing ash particles generated during combustion, in particular, played a significant role in ash deposition. Firstly, these fine ash particles
would deposit on the probe surfaces through thermophoresis and condensation mechanisms and initiate ash deposition. Secondly, these fine particles rich in Ca, S, and Na could also behave as glue and stimulate ash sintering due to its low melting points. However, the refractory ash minerals in inhibiting ash sintering, slagging and fouling were deficient in the ash samples from muffle furnace and the ash deposits. Therefore, severe ash deposition problems have been occurred in the boilers firing Zhundong lignite.

8.1.3.2 Effect of coal blending
The effect of coal blending on ash deposition during the combustion of Zhundong lignite was also investigated (Chapters 5, 6 and 7). It was found that blending Australian bituminous or Indonesian lignite into Zhundong lignite would be one mitigation strategy for ash deposition of Zhundong lignite (Chapters 5 and 6). The addition of AB or IL into ZL introduced more refractory ash particles, which not only decreased the formation of fluxing fine ash particles from ZL, but also behaved as “skeleton”, decreasing the contacts between fine ash particles and therefore inhibiting further formation of low melting-points eutectics. However, at low AB or IL ratios, this mitigation effect might not be effective as significant amount of fine ash particles remained in the ash deposits.

The effect of coal blending on the structure and chemistry of the ash deposits were also investigated (Chapter 7). The results in Chapter 7 supported the conclusions drawn from Chapters 5 and 6 that coal blending would mitigate ash deposition of Zhundong lignite due to the addition of refractory ash particles. However, the analysis on the structure and chemistry of the ash deposits also revealed that the thickness of the ash deposits increased as the AB or IL ratio increased. This is mainly because the AB or IL coal itself tended to generate more ash particles due to its high ash content, therefore allowing more ash particles to be deposited on the probe. As the deposit thickness increased, the temperature of the outer layer of the deposit might be increased, which might induce sintering or fusion at the outer layer of the deposit, and requires further investigation.

8.1.3.3 Effect of probe temperature
The effect of probe temperature on ash deposition during combustion of different coals was also investigated. It was found that the probe temperature indeed affected the ash
deposition processes and the deposit behaviour. On one hand, the condensation of sodium vapours and thermophoresis deposition of fine ash particles would be decreased, resulting in a decrease in AAEM contents in the deposits and therefore an increase in ash sintering temperature. On the other hand, however, the increase in probe temperature would aggregate ash sintering, leading to an increase in particle sizes and the mineral interactions in the ZL, ZL80AB20, and ZL80IL20 ash deposits. However, these changes were not observed in the rest ash deposits as probe temperature increased. These competitive effects minimizes the probe temperature effect and increases the difficulty in distinguishing the properties of the ash samples at different probe temperatures.

8.2 Evaluation of the experimental results

The systematic experimental and analytical work on the coal properties, ash properties, mineral transformation and interaction, ash deposits characteristics during combustion of coals with vastly different ash chemistry and mineralogy have provided a sound understanding on how coal blending and probe temperature affect the ash deposition mechanisms and the deposit behaviour. Meanwhile, the analysis of the deposit structures in Chapter 7 also permitted the analysis into the structure and chemistry of the ash deposit during combustion of Zhundong lignite. However, these results obtained in this study need to be evaluated to better comprehend the experimental work and their significances to ash deposition in practical utility boilers.

8.2.1 Coal samples

Zhundong lignite, Australian bituminous, and Indonesian lignite with vastly different ash chemistry and mineralogy were used in this study. However, this does not mean that properties of these coal samples represent coals in the whole coalfield as coals are heterogeneous in nature and their properties can vary even for the same coals. What is important in reporting a study of a coal is to provide the necessary analysis data and other information about the coal samples being studied. Analysis on the property date of the coal samples is still required and essential for understanding its deposition problems.

8.2.2 Ash samples from muffle furnace

The properties of the ash samples prepared in muffle furnace were characterised in detail and the mineral interactions in the ash samples as a function of ashing temperature were systematically analysed. However, these results can only provide limited indications to evaluate ash slagging and fouling during combustion in pulverised
coal-fired boilers as the ash samples prepared from muffle furnace are not identical to those of ash deposits. Firstly, the ash samples prepared in muffle furnace were formed at relatively lower temperatures than that in the boilers, leading to different mineral phases in the ash samples and the deposits. Secondly, burning the coal samples in muffle furnace is more like combustion in a fixed-bed boiler without considering the deposition processes, whereas ash deposition is a dynamic process where a suite of deposition mechanisms is at play. In particular, the vaporized alkali and alkali earth species during combustion would condense on the probe at low surface temperatures, allowing for the capture of Na elements in the deposit samples. However, the ash samples from muffle furnace at relatively high temperature did not undergo condensation process. Therefore, the properties of the ash samples prepared from muffle furnace are not identical to those of ash deposits.

8.2.3 Ash deposits from drop tube furnace
The ash deposits on a probe at different temperatures during combustion of coal blends were systematically characterised, allowing for the discussion on the ash deposition mechanisms and deposition behaviour of different coals and coal blends. However, ash deposition in the boiler is very complicated and can’t be completely understood using one ash sampling probe that used in the current study. Firstly, the probe temperature selected during experimentation simulating the superheater surfaces in different boilers would not be simply extrapolated to ash deposition in other heat transfer surfaces. Of particular concern is the condensation or thermophoresis deposition of alkali and alkali earth species as they are significantly temperature-dependent. Secondly, different surface geometry, orientation and impact angle are also significant for ash deposition, leading to different deposit characteristics on the heat transfer surfaces. Thirdly, the ash samples were collected in a relatively short time compared to the operating period of a boiler. This means that the findings of this study are more relevant to the initial ash deposition process. Increasing the deposition time would lead to the formation of semi-fused or fused ash deposits with the shedding of the deposits, both of which were not the aims of this study.

8.2.4 Error analysis
The quantitative analyses in this study included the determination of ash sintering temperature and ash fusion temperatures. The sintering temperature measurement with the new criterion using the pressure-drop sintering device provided an error of ±12 °C, which is accurate enough to investigate the effect of coal blending and probe
temperature on the sintering temperature of the coal ashes. The measurement of ash fusion temperatures of each sample using the ash fusion auto-analyser was repeated three times and found that the relative error was within 30 ~ 50 °C, providing a good repeatability of the results.

**8.3 Implications of the current work**

**8.3.1 Coal analysis**

Zhundong lignite, Australian bituminous, and Indonesian lignite with vastly different ash chemistry and mineralogy were used in this study. The property data of the coal samples were reported and the properties of the ash samples were analysed. These data were valuable in practical boilers burning these three coals. In addition, the analysis on the ash samples and the deposit samples from these coals and coal blends could also be extrapolated to other fuels with similar ash chemistry and mineralogy.

**8.3.2 Analysis of the muffle furnace ashes**

The systematic analysis on the ashes from muffle furnace subjecting to different combustion temperatures allowed investigation into the effect of coal blending on the sintering and fusion characteristics of the ash samples as well as the interactions between different mineral phases. The standard test on these ash samples provided basic means to evaluate the slagging and fouling propensity of the ash samples during combustion in pulverised coal-fired boilers. In addition, the ash samples were prepared in muffle furnace, which were also close to combustion in fixed-bed reactor or stock-fired furnaces. Therefore, these results and analysis also provided significant implications for ash sintering, fusion and mineral interaction in fixed-bed or stock-fired reactors.

**8.3.3 Ash deposition mechanisms**

The ash deposits formed on the horizontal probe surface, being perpendicular to the gas stream, allowed a suite of different ash deposition mechanisms to be observed and examined, including condensation (< 1 µm), thermophoresis (< 10 µm), impaction (> 10 µm) and chemical reactions. The characterisation of these ash deposits enabled the discussions and understanding of how the ash deposition was initiated, how the deposit developed and how the mineral phases in the deposits interacted. Particularly, the deposition mechanisms and deposit characteristics during the combustion of Zhundog lignite and its blends were investigated and analysed. The target geometry, orientation, and impaction angle indeed affect the deposit characteristics as ash deposition is a
selective process. Nonetheless, the present drop-tube furnace and deposition probe configuration represents a generic ash deposition process around superheater surfaces in a boiler, and allowed the initial ash deposition mechanisms and processes to be investigated.

8.3.4 Effect of coal blending
Coal blending could be one mitigation strategy for ash deposition of Zhundong lignite. Adding AB or IL coals or other coals with similar ash chemistry and mineralogy into ZL would inhibit the formation of fluxing minerals, increase the sintering temperature of the ash, and therefore mitigate ash deposition. However, the blending ratio is also critical for mitigation of Zhundong lignite ash deposition. At low AB or IL ratios, the mitigation for ZL ash deposition may be less effective as the fine ash particles generated from Zhundong lignite could not be diluted.

8.3.5 Effect of probe surface temperatures
The probe surface temperatures were controlled at 500 °C, 600 °C, 700 °C, and 750 °C, respectively, to simulate ash deposition on superheaters in subcritical, supercritical, and ultra-supercritical boilers. Results show that as probe temperature increased from 500 °C to 750 °C, ash sintering and mineral interaction between Na and aluminosilicate were facilitated during combustion of ZL, ZL80AB20, ZL80IL20 coal samples, leading to the formation of fluxing mineral phases such as hauyne and nepheline. This indicates that ash deposition on ultra-supercritical boilers burning the same coal or coal blends would be aggregated. However, ash sintering and mineral interactions of the remaining coal blends were not promoted, indicating that these ash deposits are more refractory and resistant to the temperature change and the ash deposition on superheaters in ultra-supercritical boilers could be lessened.
Chapter 9 Conclusions and Recommendations

This thesis study systematically characterised the ash samples prepared from plasma asher and muffle furnace at different furnace temperatures as well as the ash deposits formed on a probe at different probe temperatures during combustion of blended coals in a drop tube furnace, permitting analysis into the ash sintering and fusion behaviour, mineral transformation, and the ash deposition processes and mechanisms on superheaters in subcritical, supercritical and ultra-supercritical boilers. The conclusions obtained from the investigations detailed in this study have also provided insights into the effect of coal blending on ash deposition during Zhundong lignite combustion, and also enabled recommendations to be made for future work to further comprehend its ash deposition mechanisms.

9.1 Conclusions

9.1.1 Effect of coal blending on sintering and fusion characteristics and mineral transformation of ashes in muffle furnace

- The Zhundong lignite ash prepared in muffle furnace at 815 °C was rich in alkali and alkali earth contents in the forms of fluxing minerals such as anhydrite, calcium silicate and yeelimite, leading to relatively low sintering and ash fusion temperatures.

- The Australian bituminous and Indonesian lignite ashes were rich in acidic oxide in the forms of quartz or mullite, leading to relatively high sintering and fusion temperatures.

- The sintering temperature of the ash increased as the ratio of the Australian bituminous or Indonesian lignite in the blends increased. However, the softening temperature (ST) and fluid temperature (FT) of the ash of the blend firstly decreased and then increased, reaching the lowest values at the 40% Australian bituminous or 20% Indonesian lignite addition ratio. The significant variations in the ash chemistry and the mineral phases (nepheline, hauyne, gehlenite, quartz, and mullite) in the ashes were the main reasons for the variation in the ash fusion characteristics.
Chapter 9 Conclusions and Recommendations

- The physicochemical properties of the Zhundong lignite ash are significantly dependent on ashing temperature. As ashing temperature increased, the vaporisation of Na, Cl, K, and S, and the decomposition of carbonates and sulphates occurred, and the minerals in the ashes transformed from low temperature refluxing minerals to relatively refractory minerals such as calcium silicate and yeelimite. As a result, the ash sintering temperature increased as the ashing temperature in muffle furnace increased.

9.1.2 Effect of coal blending on ash deposition during combustion of Zhundong lignite

- The Zhundong lignite ash deposited on the probe at 500 °C was dominated by fluxing minerals including anhydrite, lime, hematite, and nepheline, with the presence of significant amount of fine particles (< 10 μm) and sintered particles, and had a relatively low sintering temperature and high fouling propensity. The Australian bituminous and Indonesian lignite ash deposits formed on the probe at 500 °C were dominated by refractory minerals including quartz and mullite with sizes larger than 10 μm, and had relatively high sintering temperatures and low fouling and slagging propensity.

- The addition of the Australian bituminous or Indonesian lignite to Zhundong lignite increased the amount of quartz and mullite in the deposits, and decreased the amount of fluxing minerals including nepheline. Meanwhile, as the Australian bituminous or Indonesian lignite ratio in the coal blends increased, the amount of fine particles in the deposits decreased and was further diluted by the refractory ash particles, leading to mitigated particle sintering.

- The sintering temperature of the deposit increased as the Australian bituminous or Indonesian lignite ratio increased, indicating that the severe ash deposition of Zhundong lignite could be lessened through coal blending.

9.1.3 Effect of probe temperature on ash deposition during combustion of blended coals

- For certain coal blends (ZL, ZL80AB20, ZL80IL20, ZL60IL40), mineral interactions and ash sintering on the probe were facilitated in the ash deposits as
probe temperature increased from 500 °C to 750 °C, leading to the formation of new mineral phases (hauyne or nepheline) and an increase in particle size.

- When the Australian bituminous ratio in the coal blends was higher than 40% or the Indonesian lignite ratio higher than 50%, these deposits were more refractory and more resistant to the temperature change and significant mineralogical and morphological changes were not observed.

- As probe temperature increased, the sintering temperature of the ash deposit increased. This is attributed to the differences in chemistry and mineralogy of the ash deposits owing to the variations in the condensation of sodium vapors and thermophoresis deposition of fine ash particles.

9.1.4 Effect of coal blending and probe temperature on the structure and chemistry of the Zhundong lignite ash deposits

- The analysis into the structure and chemistry of the Zhundong lignite ash deposit at 550 °C revealed that the low melting points anhydrite, lime, and hematite ash particles with sizes less than 25 µm initiated Zhundong lignite ash deposition. These fine ash particles also dominated the ash deposits as deposit further accumulated.

- Sulphation of calcium occurred on the probe and the sulphation degree increased as the deposition time increased. Meanwhile, the sulphation of calcium was promoted as probe temperature increased from 550 °C to 750 °C, resulting in an increase in the S/Ca ratio of the fine particles.

- The effect of coal blending on the structure and chemistry of Zhundong lignite ash deposit was investigated. The introduction of refractory ash particles from Australian bituminous or Indonesian lignite diluted the existing fine ash particles, making the deposit less sticky than the Zhundong lignite ash deposit, and therefore mitigated ash deposition of Zhundong lignite.

- The addition of kaolin introduced more mullite ash particles in the deposit at probe temperature of 600 °C and inhibited the sulphation of calcium. The use of
Chapter 9 Conclusions and Recommendations

Bauxite showed a dilution effect and also mitigated Zhundong lignite ash deposition.

- The structure and chemistry of the ash deposits of Zhundong lignite and water-washed Zhundong lignite did not show significant difference from the SEM-EDS analysis. This means that the effectiveness of water washing on ash deposition warrants further and quantitatively investigation.

9.2 Recommendations

Although this study has vastly advanced the understanding of the thermal behaviour of the ash and the deposition characteristics during combustion of blended coals, it also highlights that more work can be done to obtain further understanding of the ash deposition mechanisms in the boiler to mitigate ash deposition during Zhundong lignite combustion.

This research has looked into the mineral transformation and interactions of the ash sample as a function of combustion temperature in muffle furnace and a function of blending ratio, explaining the sintering and fusion characteristics of the ash. However, it is also evident that the evaporation of alkali and alkali earth metals occurred during heating, resulting in the loss of AAEM contents. It is therefore recommended to investigate how much AAEM contents were retained in the ash, how much AAEM contents escaped during the combustion at high temperatures, and how the evaporated AAEM interact with char and ash etc.

The data obtained from the current work on the mineral matter in Zhundong lignite and ash deposits has also provided understanding on ash formation and deposition during Zhundong lignite combustion. The characterisation of the ash deposits on the deposition probe permitted analysis on the mineral interactions of different ash particles and the sintering/fouling propensity of the deposit. To better understand the ash deposition behaviour, the deposit thickness, deposition rate, and the thermal conductivity of the ash deposits are needed to further evaluate the ash deposition characteristics. In addition, the ash deposits formed on the probe only represented the initial ash deposition stage where ash slags were not formed. The formation and analysis of the ash slags are also recommended in future work to understand the slagging characteristics of the deposits.
References


Akiyama K., Pak H., Ueki Y., Yoshiie R. & Naruse I. 2011, Effect of MgO addition to upgraded brown coal on ash-deposition behavior during combustion. Fuel, 90, (11), 3230-3236.


Bai J., Li W., Li C., Bai Z. & Li B. 2009, Influence of coal blending on mineral transformation at high temperatures. Mining Science and Technology (China), 19, (3), 300-305.


References


Jak E., Degterov S., Hayes P.C. & Pelton A.D. 1998, Thermodynamic modelling of the system Al₂O₃ · SiO₂ · CaO · FeO · Fe₂O₃ to predict the flux requirements for coal ash slags. Fuel, 77, (1–2), 77-84.


Luan C., You C. & Zhang D. 2014, Composition and sintering characteristics of ashes from co-firing of coal and biomass in a laboratory-scale drop tube furnace. Energy, 69, (0), 562-570.


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References


References


References


Zhang J., Zhang L., Yang Z., Yan Y., Mao Y. & Bi J. 2015, Effect of bauxite additives on ash sintering characteristics during the K2CO3-catalyzed steam gasification of lignite. RSC Advances, 5, (9), 6720-6727.


Appendix

Appendix I

Mineral phases in coal and their morphologies, size distribution, possible origin, and concentrations: M—major, m—minor, A—accessory, (<0.5%); D—detrital, S—syngenetic, E—epigenetic, AU-authigenic; ●—dominant, ○—subordinate; P-proportion. Size distribution may be different due to their various determination methods.

<table>
<thead>
<tr>
<th>Phase-mineral</th>
<th>Formula</th>
<th>Origin</th>
<th>Size and morphology</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Size and morphology</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D—angular or semi-rounded grains, clusters, 0.2 µm - 1 mm;</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO₂</td>
<td>M</td>
<td>● ○ ○</td>
<td></td>
</tr>
<tr>
<td>Cristobalite</td>
<td>SiO₂</td>
<td>A-m</td>
<td>● ○ ○</td>
<td></td>
</tr>
<tr>
<td>Opal</td>
<td>SiO₂·nH₂O</td>
<td>A-m</td>
<td>○ ○ ●</td>
<td></td>
</tr>
<tr>
<td>kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>M</td>
<td>● ● ○</td>
<td>Layers, lenticles, lenses</td>
</tr>
<tr>
<td>Illite</td>
<td>(K,H₂O)Al₂(Al, Si)Si₃O₁₀ (OH)₂</td>
<td>A-M</td>
<td>● ● ○</td>
<td>Layers, lenticles, lenses</td>
</tr>
</tbody>
</table>

Clay minerals, some fine clay aggregates associated with pyrite, feldspar,
<table>
<thead>
<tr>
<th>Phase-mineral</th>
<th>Formula</th>
<th>Content</th>
<th>Origin</th>
<th>Size and morphology</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite</td>
<td>((\text{Na,Ca})<em>{0.3}(\text{AlMgFe})</em>{2}\text{Si}<em>4\text{O}</em>{10} (\text{OH})_2\cdot x\text{H}_2\text{O})</td>
<td>m</td>
<td>D</td>
<td>Layers, lenticles, lenses</td>
<td>gypsum, and glass</td>
</tr>
<tr>
<td>Biotite</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-feldspar</td>
<td>(\text{KAlSi}_3\text{O}_8)</td>
<td>A~M</td>
<td>●</td>
<td>Angular to semi-rounded grains, prismatic crystals with a length up to 120 µm</td>
<td>Commonly weathered by clay minerals</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>(\text{NaAlSi}_3\text{O}_8\text{–CaAl}_2\text{Si}_3\text{O}_8)</td>
<td>m-M</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td>(\text{KAl}_2\text{Si}<em>3\text{O}</em>{10} (\text{OH})_2)</td>
<td>m</td>
<td>●</td>
<td>Flakes 0.5-150 µm</td>
<td>Mica, mainly associated with feldspar in clay-rich layers; Unstable</td>
</tr>
<tr>
<td>Biotite</td>
<td></td>
<td>m</td>
<td>●</td>
<td>Flakes 0.5-150 µm</td>
<td>Mica, mainly associated with feldspar in clay-rich layers</td>
</tr>
<tr>
<td>Chlorite</td>
<td>((\text{MgFe})_3\text{Al}_5\text{Si}<em>4\text{O}</em>{10} (\text{OH})_8)</td>
<td>m</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td>((\text{NaCa})_2(\text{Mg,Fe,Al})_3 (\text{Si,Al})<em>8\text{O}</em>{22} (\text{OH})_2)</td>
<td>A~m</td>
<td>●</td>
<td></td>
<td>Refractory minerals</td>
</tr>
<tr>
<td>Mullite</td>
<td></td>
<td>A</td>
<td>●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase-mineral</td>
<td>Formula</td>
<td>Content</td>
<td>Origin</td>
<td>Size and morphology</td>
<td>Other characteristics</td>
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<tr>
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</tr>
<tr>
<td><strong>Oxides and hydroxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe₂O₃</td>
<td>A~m</td>
<td>● ○ ○</td>
<td>Pseudohexagonal, 1-5 µm crystals, flakes and ‘roses’</td>
<td>Pseudomorphic on jarosite and other iron sulphates</td>
</tr>
<tr>
<td>Diaspore</td>
<td></td>
<td>A~m</td>
<td>● ○ ○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe²⁺Fe³⁺O₄</td>
<td>A</td>
<td>●</td>
<td>Angular to semi-rounded grains; octahedral crystals, 1-10 µm in length; spheres about 10-30 µm in size</td>
<td>Dispersed in organic matter</td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td>A~m</td>
<td>●</td>
<td>Prismatic and isometric crystals or spheres in ranges of 0.1-10 µm</td>
<td>Commonly in vitrinite and clay layers</td>
</tr>
<tr>
<td>Brucite</td>
<td>Mg(OH)₂</td>
<td>A~m</td>
<td>○ ●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boehmite</td>
<td></td>
<td>A~m</td>
<td>● ○ ○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Goethite</td>
<td>α-FeOOH</td>
<td>A~m</td>
<td>● ○ ○</td>
<td>Crusts of fine-grained flakes up to 10 µm</td>
<td>Associate with hematite</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al(OH)₃</td>
<td>A</td>
<td>● ○ ○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td></td>
<td>A~m</td>
<td>● ○ ○</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corundum</td>
<td></td>
<td>A</td>
<td>●</td>
<td>Short prismatic crystals about 0.3 µm in length</td>
<td></td>
</tr>
</tbody>
</table>
### Appendix

<table>
<thead>
<tr>
<th>Phase-mineral</th>
<th>Formula</th>
<th>Origin</th>
<th>Content</th>
<th>Size and morphology</th>
<th>Other characteristics</th>
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<tbody>
<tr>
<td><strong>Carbonates</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃</td>
<td>A~M</td>
<td>● ● ●</td>
<td>Individual grains, ‘roses’ and lenses, prismatic crystals</td>
<td>E-calcite veinlets, filling cavities, as a cement of fractured coal fragments</td>
</tr>
<tr>
<td>Dolomite</td>
<td>CaMg(CO₃)₂</td>
<td>A~M</td>
<td>○ ● ●</td>
<td>Rhombohedral crystals 0.4-10 µm long</td>
<td></td>
</tr>
<tr>
<td>Siderite</td>
<td>FeCO₃</td>
<td>A~M</td>
<td>● ● ●</td>
<td>Massive, fine grained lenses, nodules and layers, spheroidal aggregates;</td>
<td>The centre of spheroidal aggregates is ankerite</td>
</tr>
<tr>
<td>Ankerite</td>
<td>Ca(Mg, Fe)(CO₃)₂</td>
<td>A~M</td>
<td>● ○ ●</td>
<td>Rhombohedral crystals 0.4-10 µm long;</td>
<td></td>
</tr>
<tr>
<td>Magnesite</td>
<td></td>
<td>A~m</td>
<td>○ ○ ●</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aragonite</td>
<td></td>
<td>A~m</td>
<td>○ ○ ●</td>
<td>Massive kryptomere and it infills fissures thickness up to 20 µm</td>
<td></td>
</tr>
<tr>
<td><strong>Sulphides sulphosalts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>m-M</td>
<td>● ○ ●</td>
<td>S-pyrite: frambois of octahedral and angular grains in the range of 10-20 µm; octahedral and cubic-octahedral crystal of 1-30 µm, angular to semi-rounded grains in organic matrix; clusters, layers; E-pyrite: rims, octahedral crystals up to 10 µm, massive veinlets</td>
<td></td>
</tr>
</tbody>
</table>
## Appendix

<table>
<thead>
<tr>
<th>Phase-mineral</th>
<th>Formula</th>
<th>Content</th>
<th>Origin</th>
<th>Size and morphology</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marcasite</td>
<td>FeS₂</td>
<td>A-m</td>
<td>●</td>
<td>●</td>
<td>S-marcasite: framboids in the range of 10-150 μm, made up of prismatic crystals and penetrated twins; grains, flakes and prismatic crystals with spear-like form and 20-70 μm long; E-marcasite: spheroidal aggregates in the range of 100-300 μm; compact veinlets; kryptomere;</td>
</tr>
<tr>
<td>Purrhotite</td>
<td>Fe₁₋ₓS</td>
<td>A~m</td>
<td>●</td>
<td>○</td>
<td>Angular, 30-50 μm grains in magnetic fraction</td>
</tr>
</tbody>
</table>

### Sulphates

<table>
<thead>
<tr>
<th>Phase-mineral</th>
<th>Formula</th>
<th>Content</th>
<th>Origin</th>
<th>Size and morphology</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>A-M</td>
<td>○</td>
<td>●</td>
<td>Crusts, lenses or infilling cracks; Long-prismatic crystals with a length up to 2-3 mm; penetrated twins, or radical, fan-shaped aggregates up to 0.5 cm</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO₄</td>
<td>A</td>
<td>●</td>
<td></td>
<td>Commonly associated with pyrite and marcasite; Either weathering product of sulphide and carbonate minerals or deposit with E-sulphide</td>
</tr>
<tr>
<td>Jarosite</td>
<td>KFe₃(SO₄)₂(OH)₆</td>
<td>A-m</td>
<td>○</td>
<td>●</td>
<td>Colloform crusts and aggregates of prismatic and wedge-shaped crystals or crystals twins; ‘roses’ typically about 20-30 μm in size</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maybe a weathering product of pyrite and marcasite framboids</td>
</tr>
</tbody>
</table>
## Appendix

<table>
<thead>
<tr>
<th>Phase-mineral</th>
<th>Formula</th>
<th>Origin</th>
<th>Size and morphology</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alunite</td>
<td>A~m</td>
<td>o</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Hexahydrate</td>
<td>A~m</td>
<td>o</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td>BaSO₄</td>
<td>a~m</td>
<td>o  ●</td>
<td>Aggregates of prismatic grains up to 50 µm</td>
</tr>
<tr>
<td><strong>Phosphates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca₅(PO₄)₃(F,Cl,OH)</td>
<td>a~m</td>
<td>●  o  o</td>
<td>Prismatic crystals with a length of 0.1-20 µm Commonly contains gas-liquid inclusions</td>
</tr>
<tr>
<td>Vivianite</td>
<td>A~m</td>
<td>o</td>
<td>o</td>
<td></td>
</tr>
<tr>
<td>Goyazite</td>
<td>A~M</td>
<td>o</td>
<td>o</td>
<td></td>
</tr>
<tr>
<td><strong>Chlorides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sylvite</td>
<td>KCl</td>
<td>a</td>
<td></td>
<td>Cubic crystals in the range of 3-10 µm, clusters</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
<td>a</td>
<td>o  ●</td>
<td>Cubic crystals in the range of 3-10 µm, clusters</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminosilicate</td>
<td></td>
<td>A~m</td>
<td>●</td>
<td>Spheres, spheroids and angular particles in the range 1-40 µm, commonly containing gas bubbles about 0.1-0.3 µm in size Individually exists in organic matrix</td>
</tr>
<tr>
<td>volcanic glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous phase</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>