Slagging behaviour of Australian brown coals and implications for their use in gasification technologies

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Alexander Y. Ilyushechkin, Daniel Roberts

CSIRO Energy, Australia

ABSTRACT

Utilisation of brown coal in slagging gasification technologies requires a detailed assessment of coal ash chemistry in terms of potential slagging behaviour. We investigated the phase compositions of four categories of brown coal ashes and synthetic slags after processing at 900–1100 °C and 1200–1600 °C, respectively, under reducing conditions similar to those used in coal gasification. We also determined the ash fusion temperature (AFT) of ashes and slag viscosity, and discuss these in terms of ash and slag compositions.

It is found that the liquid phase appearance at low processing temperatures (900–1100 °C) strongly depends on ash mineral composition and primary phase field of the bulk composition. However, the ash compositions are not in phase equilibria, as well as liquid phase appears at temperatures lower than the AFT's. Slags processed at high temperatures (1200–1600 °C) generally follow phase equilibria, although some differences in calculated and observed compositions were identified.

For practical applications in gasification technologies, ash with high silica and/or high-alumina compositions may suit entrained-flow gasifiers. Some of these ashes require fluxing or an adjustment to the silica:alumina ratio to obtain suitable slag viscosity. Coals from high-iron–magnesium ash and high-calcium ash are more suitable for use in non-slagging gasifiers.

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1. Introduction

The past decade has seen increased interest in the use of low-rank Australian brown coal (also known as lignite) in technologies that are more environmentally friendly than combustion-fired power plants. One potential option is gasification, in which the coal is used as a feedstock to produce syngas. The syngas can then be converted to liquid fuels and chemicals. Gasification technologies include fixed or moving beds, fluidised beds and entrained-flow systems, while two common gasification atmospheres – air or oxygen – provide a variety of parameters and operational conditions.

Oxygen-blown gasification is expected to be more suitable to produce chemicals from syngas than air-blown gasification. As brown coal is highly reactive, it is well suited for use in fluidised-bed gasifiers, but agglomeration or slagging of the coal minerals must be avoided [1, 2]. This could be an issue when using brown coal in fluidised beds; therefore, oxygen-blown entrained-flow gasification is being considered.

Knowledge of the mineral matter behaviour of the feedstock at various gasification operating conditions is required to match the feedstock to the optimal gasification technology. Typically, coal with high AFT will suit non-slagging fixed beds and fluidised-bed gasifiers. For coals that demonstrate low ash content and low AFT (below 1400 °C), entrained-flow gasification is preferable. Entrained-flow gasifiers require slag viscosity to be within the range of 5–25 Pa·s at these temperatures to achieve steady slag tapping [3]. Although slagging characteristics strongly depend on coal mineral and chemical composition, very few studies of brown coal slagging behaviour and characteristics have been undertaken under different gasification conditions, including entrained-flow gasification [4,5]. No systematic studies have been done to indicate the best option for gasification of specific brown coals in terms of their mineral matter behaviour.

One of the reasons for the lack of studies is the large variation in brown coal ash compositions. Over the past three decades, Victorian brown coal analysis and coal ash chemistry has been presented in a number of papers [6–14]. The coal ash compositions of three of the most well-known Australian brown coals are listed in Table 1. These are Loy Yang, Yallourn, and Morwell (also known as Hazelwood), which are all located in the Gippsland Basin, Latrobe Valley region of Victoria.

To identify the common features of brown coal slagging behaviour associated with ash chemistry, the typical ash compositions can be grouped as:

(1) high iron (up to 48 wt.% as Fe_2O_3) and magnesium (up to 35 wt.% as MgO)
(2) high silica (up to 70 wt.% as SiO_2)

E-mail address: alex.ilyushechkin@csiro.au (A.Y. Ilyushechkin).

Table 1
Compositional range of Australian brown coal ashes (wt.%) from Latrobe valley.

Ash	Yallourn	Morwell	Loy Yang
LOI, %	1–3	1.3–4	2–5
SiO_2	1–15	2–14	5–75
Al_2O_3	2–6	1.5–4	13–28
Fe_2O_3	34–49	10–30	4–14
CaO	6–12	15–35	1–8
MgO	14–36	9–24	3–15
Na_2O	3–13	3–5	2–20

(3) high calcium (up to 32 wt.% as CaO)
(4) high aluminium (up 30 wt.% as Al_2O_3).

Category 1 is typical for Yallourn and some Morwell coals. Category 2 and 4 coal ashes can be found in Loy Yang coal, but their silica and alumina content varies significantly. Category 3 is the most typical for Morwell coal. The slagging behaviour of coal ashes from these four categories is the main focus of this study. Significant amounts of sulfur (up to ~25 wt.%) and sodium (up to ~20 wt.%) are also found in Australian brown coal ashes, but we have not grouped the ashes on the basis of these elements. Sulfur is almost absent in gasification slags, because it appears in gaseous forms, mainly as H_2S under gasification conditions; the effect of sodium on slagging behaviour is more complex and will be considered in a separate publication.

In this paper, we present the results of systematic experimental and thermodynamic modelling studies on the slag characteristics of selected Australian brown ashes. Coal ashes and slags representing the above categories were processed in a laboratory drop-tube furnace and viscosity rig at temperature ranges typical for fixed-bed and entrained-flow gasification. We also compared slag phase compositions obtained by slag quenching and subsequent microstructural analysis with calculated phase equilibria using thermodynamic modelling tools. Slag viscosity at 1200–1600 °C was measured and is discussed in terms of slag chemical and phase compositions.

2. Experimental

2.1. Ash and slag preparation

Three samples of brown coal ash were prepared by ashing coal at 780 °C for 20 h in a muffle furnace. For the 'low-temperature' ash composition study, the ashes were then placed in a molybdenum (Mo) envelope and heat treated in a drop-tube furnace at 900, 1000, and 1100 °C for 5 h in graphite lining and under a neutral atmosphere (N_2 flow) to provide reducing conditions.

Slag samples with bulk compositions that reproduced ash chemical composition (previously reported [11–13] as well as those obtained in present study) without sulfur were prepared by mixing laboratory or analytical grade Al_2O_3, CaO, Fe_2O_3, K_2CO_3, MgO, Na_2CO_3, SiO_2 and TiO_2 powders. The mixtures were pelletised and placed in Mo envelopes pre-melted at 1500–1600 °C, slow cooled (1 °C/min) to 1200–1500 °C, then kept at this temperature for 1 h before being quenched.

2.2. Sample analysis

Bulk compositions of ashes and slags were determined by X-ray fluorescence according to ASTM D3174-12 standard, and are listed in Table 2. Real coal ashes are presented in three categories, except for high calcium, where the ash sample was not available. All four categories are represented by slag samples S1–S8.

The ash fusion test was carried out in reducing atmosphere according to the ASTM D-1857-87 standard. The phase composition of ash samples was identified using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with electron probe microanalysis (EPMA). However, most of the ashes have fine dispersed microporous phases, the composition of which is difficult to determine by EPMA. XRD may confirm some of the phases, but some phases have identical peaks and are difficult to distinguish. This results in some uncertainty in the analysed phase composition and broad description of the ashes.

Quenched slags were examined using a SEM backscattering mode. EPMA was only used to identify slag phase composition, since the samples have distinctive and dense solid and liquid phases, the composition of which can be easily determined. Although iron is present as Fe^{2+} and Fe^{3+} in samples processed under different atmospheres, EPMA was used to obtain information on the total iron concentration only. The oxidation states of iron in various phases were not measured, and were instead estimated to be Fe^{2+}: Fe^{3+} = 9:1 according to thermodynamic assessment of the reducing conditions used in this study.

Phase compositions of ashes and slags were calculated using the FactSage (version 6.4) thermodynamic phase equilibria package with selected FACT53 and FToxid solid solutions and compounds [15].

2.3. Slag viscosity

Viscosity was experimentally determined in a Haake 1700 rotating bob viscometer, following the procedure described in details elsewhere [16]. Before measurements were taken, the slag was pre-melted in a Mo crucible at 1500–1550 °C for 5–6 h. To ensure reducing conditions, the viscometer was purged with a nitrogen flow of 200 ml/min and the sample was surrounded by a sacrificial graphite lining. At temperatures between 1200 and 1450 °C, P_{O_2} values near the slag surface were between 2.8×10^{-11} and 2.9×10^{-9} atm [16]. After pre-melting, the

Table 2
Bulk composition of brown coal ashes and slags used in this study (wt.%).

Ash/slag	Source	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	Mn_3O_4	BaO	SO_3
High iron–magnesium												
A1	Coal ash	3.9	1.7	44.7	7.2	18.3	5.2	0.4	0.1	0.5	0.9	16.6
S1	From A1	5.8	2.1	54.2	8.7	22.2	6.4	0.5	0.1	0.4	0.8	<0.1
S2	[11]	14.9	4.9	39.0	9.8	27.0	3.8	0.2	0.5	<0.1	<0.1	<0.1
High silica												
A3	Coal ash	76.7	10.3	3.6	1.1	2.2	1.8	0.4	1.0	<0.1	0.1	2.8
S3	From A3	79.1	10.6	3.7	1.1	2.2	1.8	0.4	1.0	<0.1	<0.1	<0.1
S4	[12]	59.9	21.7	4.9	1.7	3.8	4.9	1.4	1.6	<0.1	<0.1	<0.1
S5	[13]	50.5	15.9	9.1	7.7	9.7	5.1	0.6	1.3	<0.1	<0.1	<0.1
High calcium												
S6	[12]	21.2	5.5	23.5	31.1	13.8	3.9	0.5	0.5	<0.1	<0.1	<0.1
High alumina												
A7	Coal ash	16.4	26.5	12.9	4.1	8.5	9.6	0.3	0.6	0.1	0.2	19.3
S7	From A6	20.8	33.6	16.4	5.1	10.8	12.2	0.4	0.7	<0.1	<0.1	<0.1
S8	[13]	29.3	37.0	7.6	6.9	12.8	5.0	0.3	1.0	<0.1	<0.1	<0.1