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A REVIEW OF MINERAL MATTER ISSUES IN COAL GASIFICATION

RESEARCH REPORT 60

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CONTEXT STATEMENT

This review was prepared for CCSD to clarify the current situation with the understanding of the effects of mineral matter in coal on the gasification technology. The necessity of this review was mostly determined by the coming completion of the large program on the studies of slag flow behaviour of Australian coals. At these circumstances it is important to understand what is the state-of-the art knowledge of the effects of mineral matter in coal on slag flow behaviour and to identify the whole spectrum of the problems in gasification related to the mineral matter in coal. Therefore, this review is a part of a strategic decision-making process to determine the next priorities in the CCSD supported research in this area.

SUMMARY

The increase in demand for clean energy systems makes gasification-based technologies amongst the most prospective of the emerging power generation options. Integrated Gasification Combined Cycle (IGCC) based power stations combine the advantages of relatively cheap fuel with the efficiency and environmental performance of gas turbines. Due to the high temperature of operation of entrained flow gasifiers, coal mineral matter is required to melt and flow out of the gasifier. Whilst the requirements of the coal mineral matter in pf power stations is well known, the issues of mineral matter related to coal gasification technologies are less well understood and are the subject of recent and ongoing research interest.

This report reviews industrial relevance and the current situation for the following effects of mineral matter in coal on the gasification technologies:

- I. Issues related to the operation of the gasifier, e.g. slag flow behaviour
- II. Issues related to the reliability of gasifier, e.g. slag–refractory interactions
- III. Issues related to environmental impact, e.g. slag stability and disposal.

The ability to remove slag in gasifier tapping systems is a key factor in determining the suitability of a coal for use in entrained flow gasification technologies. Slag flow behaviour is characterised by two major parameters: slag viscosity and temperature of critical viscosity (T_{CV}). These depend largely on slag composition. Slag flow behaviour issues (assessing, predicting and controlling through coal fluxing or blending) have been addressed for the gasification of Australian coals. The remaining areas in this field (in the order of importance) are:

- Validation of existing slag flow models with existing experimental data

- Developing a T_{CV} prediction tools on the basis of a slag phase composition
- Integration of these slag flow models into robust industry tools to assess coal performance
- Developing a slag flow behaviour model explaining the phenomenon, rather than simply describing it by a large number of empirical coefficients.

Knowledge of the above areas, combined with outcomes from the recently-completed CCSD experimental program on slag flow behaviour for a wide range of Australian coals, will allow optimisation of coal fluxing and/or blending strategies for use of a range of coals in entrained flow gasification technologies.

Another important issue is slag–refractory interactions. The service life of refractory protection liners depend on the rate of reaction between slag and refractory. Mechanisms of refractory degradation are quite complicated, involving both chemical corrosion and mechanical erosion by slag. The rate of these processes depends on slag and refractory compositions and slag flow behaviour. To properly understand and resolve issues in this area, systematic studies of the effects of chemical compositions on the rate and nature of refractory degradation are required.

The experimental work in this area must be combined with modelling of slag–refractory interactions. This program should aim to match the gasifier refractory with the Australian coal slag compositions that substantially increase gasifier reliability and minimise operation expenses. As the first step, it is recommended to develop a research program for the slag–refractory interactions, concentrating on the effects of composition on slag corrosivity.

The environmental implications of producing large volumes of slag from coal gasification were also explored in this review. Slag is a stable material, to the extent that further studies in the area of contamination from leachate are not required. However, being relatively stable by itself, slag may contain some chromia inclusions from the refractory lining, which could be a potential environmental hazard. Therefore some preliminary studies on chromia inclusions in gasifier coal slags should be done in conjunction with the slag refractory interactions research. These limited studies will assess the extent of this potential issue and inform decisions on the necessity of further studies.

1. INTRODUCTION

1.1. Gasification for Energy Production

Recently there has been a significant increase in demand for more efficient and environmentally cleaner technologies for energy production. Traditionally, worldwide coal based power stations still generate a significant amount of electricity. While the world electricity demand will at least double in the next 30 years, the quota of coal based power is expected to remain the same. Therefore the coal consumption, and hence CO₂ emissions from coal, will also double in the next 30 years. The quota of coal based energy varies from country to country, with the biggest coal consumers China, India and US (for example American Energy Production Co generates annually 38,000 MWt of power, of which 72% is coal based). This reliance on coal means innovative technologies are required to increase power generation efficiency and decrease emissions of greenhouse gases.

Integrated gasification-combined cycle (IGCC) power generation technology is one of the prospective avenues for development of clean coal power generation. It combines the advantages of relatively cheap fuel (coal) with the efficiency of gas turbines, reducing coal consumption per energy unit production. Also IGCC technology when compared with the conventional pf-combustion technologies, provides better environmental performance by reducing hazardous (SO_x, NO_x etc.) and greenhouse gas (CO₂) emissions and allowing a decrease in coal consumption.

In IGCC technology, carbonaceous feedstock is converted into useful gaseous products, which are then used to generate electricity. Burning of coal with reduced quantities of oxygen (ie lower than that used in conventional pf combustion technologies) and steam converts coal into synthesis gas or 'syngas', a mixture of predominantly CO and H₂. Heat required for this process is provided by partial combustion of the feedstock. Gasifiers operate under high temperature and pressure to increase reaction intensity and therefore coal throughput and to provide a high pressure fuel gas to the gas turbine system.

In current gasification technologies, the syngas produced is used firstly to run a gas turbine (to utilise its high pressure and temperature). The heat from this system is then used to run a second (steam) turbine. In the future it is envisaged that during 'peak hours' syngas will be used for electricity generation, at other time syngas could be converted into liquid fuels, hydrogen and/or other chemical products (eg clean diesel fuel, H₂). This concept of 'polygeneration' provides more flexibility and has potential to become a fundamental part of the future hydrogen economy.

This review will focus on the gasifier component of IGCC systems, in particular on the impacts of feedstock with mineral matter on the operation of these gasifiers.

1.2. Types of Coal Gasification Technologies

There is a range of different types of gasifiers (Figure 1). They can be categorised into three main groups on the basis of their flow geometry: fluidised bed; fixed or moving bed; and entrained flow gasifiers [1]

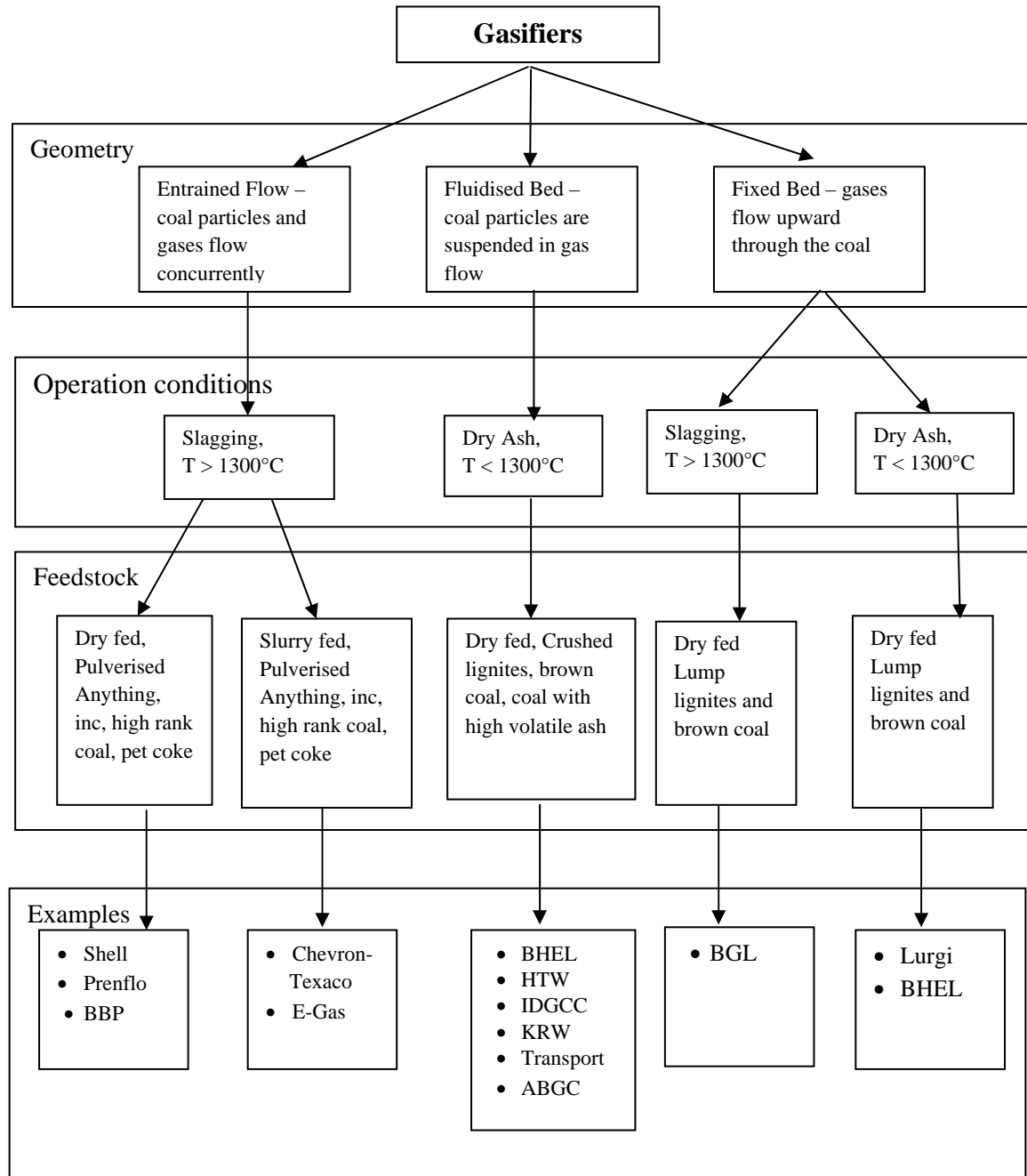


Figure 1: Different types of commercially available coal gasification technologies

1.2.1. Fluidised Bed Gasifiers

In fluidised bed gasifiers, feedstock coal particles (0.5–5 mm) are suspended in a bed of sand or other material (including coal ash) which is fluidised by the gas flow. They operate on a dry crushed feedstock at low operating temperatures (600–1000°C). To avoid ash agglomeration (which causes uneven bed fluidisation) the process coals must have an ash fusion temperature (AFT) higher than the operating temperature of the gasifier.

Since these systems can operate at relatively low temperatures, they are suitable for reactive coals such as lignites and brown coals (since they can achieve satisfactory conversion) or for coals containing potentially troublesome volatile inorganic compounds (to avoid highly reactive and corrosive vapours). Because of their low operating temperatures and the need to avoid agglomeration in the bed, none of them operates in a slagging mode and all discharge mineral matter as dry ash.

1.2.2. Fixed Bed Gasifiers

In a fixed bed gasifier gases flow upward through the bed of feed coal (particle size is typically 5–80 mm). They could be either low temperature dry ash or slagging gasifiers. The dry ash gasifiers have nearly the same requirements for the coal ash properties as for fluidised bed gasifiers. The requirements of the mineral matter in coals for slagging fixed bed gasifiers are similar to those for blast furnaces. The latter are relatively well understood and are not discussed in this review.

Slagging fixed bed gasifiers are highly sensitive to the coal reactivity (due to the large size of feed coal particles they favour highly reactive coals) and to physical strength and coking behaviour of coal particles to maintain the permeability of the fixed bed. This sensitivity implies stringent requirements to the coal specifications. Due to their relatively small throughput and very limited variations in coal specifications, the export market of Australian coals for this type of gasifiers is unlikely to grow in the near future.

1.2.3. Entrained Flow Gasifiers

In entrained flow gasifiers gases and coal particles flow concurrently. This configuration typically implies a short residence time of coal particle inside the reaction zone, approximately 5–10 s. This short residence time, consequently, requires coal to be pulverised to ensure high carbon conversion. Also, to maximise the rate of carbon conversion, entrained flow gasifiers are designed for high operating temperatures, with flame temperatures above 1800°C.

The entrained flow gasifiers allow both high coal throughput and usage of wide range of less reactive high rank coals, due to their intense reaction conditions. This

characteristic makes the entrained flow gasifiers the most prospective for the market of Australian bituminous and sub-bituminous coals for both national and world power generation industry.

Depending on their design, entrained flow gasifiers can accept either dry or slurry fed fuel (Figure 1). Additional energy (obtained from combustion of some of the coal) requirements to evaporate water in slurry-fed gasifiers makes the dry-fed gasifiers more coal efficient and less oxygen consuming. On the other hand, the coal fed systems for dry fed gasifiers are more complicated to build and operate than the slurry-fed devices. Because of this complication, dry fed gasifiers generally operate at lower pressures (up to 4 MPa), compare to slurry-fed systems (7 MPa). The higher operating pressure is beneficial to increase reaction intensity and reduce gasifier size. Higher operating efficiency of dry-fed gasifiers is challenged by simpler and cheaper design of feeding systems and higher operating pressures of slurry-fed gasifiers.

Due to the high temperatures (above ash fusion temperature, AFT) the coal mineral matter melts and is removed through a slag tap system. All of the commercial entrained flow gasifiers are slagging gasifiers. Each of the entrained flow gasifier technologies, depending on their design, has slightly different requirements for the coal mineral matter.

Gasifiers with water cooled steel (e.g. Shell) or refractory (e.g. BBP, EAGLE) walls rely on a slag layer to protect the walls and minimise heat loss through the wall. For these cooled wall gasifiers, there is a minimum ash content requirement (from 1 % for BBP technology to about 8 wt % for Shell gasifiers).

In the other common entrained flow gasification designs (e.g. Texaco, Destec), the inner gasifier walls are lined with a refractory. This lining provides better thermal insulation and allows operating on low ash feedstock, like petroleum coke. However, this lining is susceptible to corrosion and erosion by flowing coal slag. Some of the compounds which are present in coal slag (e.g. SiO_2 , CaO , FeO) can react with refractory walls and/or dissolve them. Slag may also penetrate deep into the refractory causing cracks which can lead to material loss.

For both types of gasifier there are also limitations on the maximum content of the ash. This tolerance to maximum ash content depends not only on gasifier design, but also other factors such as available infrastructure and cost of slag storage and disposal. The maximum ash content for entrained flow gasifiers varies from 12 to 40 wt% (on dry coal basis).

Smooth operation of an entrained flow gasifier depends on the steady removal of slag through a slag tap device. The success of this tapping depends on the flow behaviour of slag, which can be characterised by two main parameters. The first of these

parameters is the temperature dependence of slag viscosity. Usually viscosity is exponentially proportional to inverse temperature; however at a certain temperature, very small changes in temperature ($\sim 5^{\circ}\text{C}$) can result in large changes in viscosity. This temperature is called a temperature of critical viscosity (T_{CV}) and is the second important parameter used to describe slag flow behaviour (Figure 2). The nature of such a phenomenon is related to the crystallization of the solid phase from the melt, which, in turn, affects the slag viscosity behaviour. The exact relations are yet unclear and requires further studies [7]. It should be noticed that T_{CV} may not be observed for every slag composition.

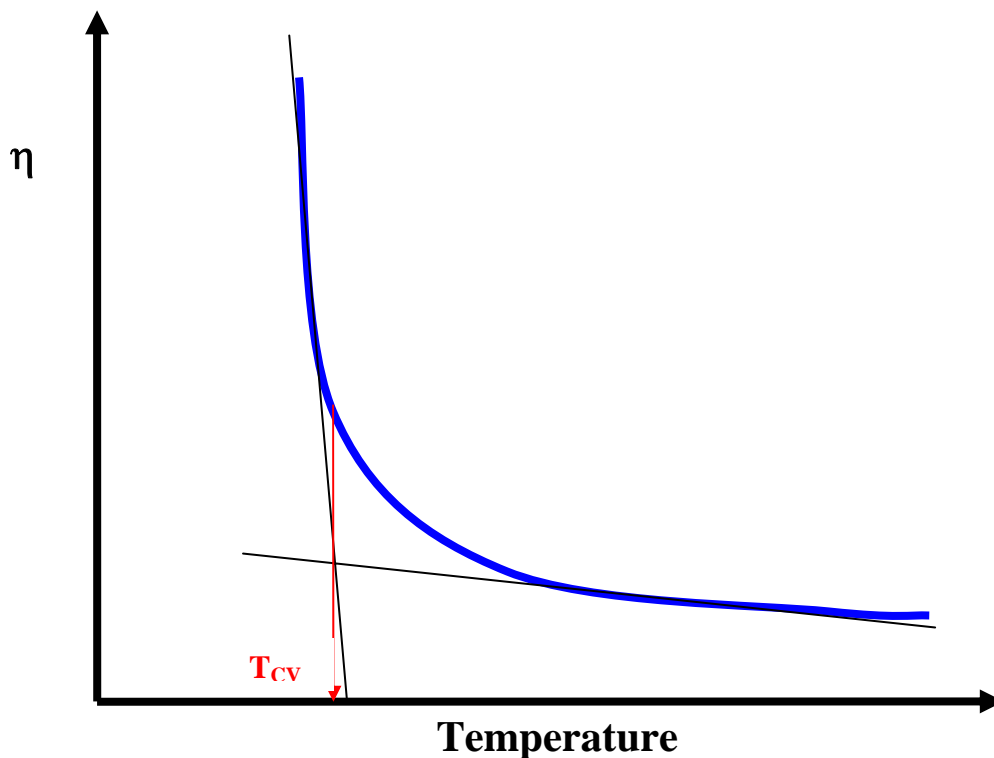


Figure 2: Schematic diagram of the definition of Temperature of critical viscosity (T_{CV})

To achieve steady slag tapping in entrained flow gasifiers, slag viscosity at the temperature of the tap (usually $1400\text{--}1500^{\circ}\text{C}$) should be within a range from 5 to 25 Pa s, with an optimum value of 15 Pa s [2-5]. Furthermore, gasifier operation temperature should be above the slag's T_{CV} . Viscosity and T_{CV} strongly depend on slag composition. To increase the range of coals that can be used in entrained flow gasifiers it is common practice to blend the feedstock with either a flux or with other coals with suitable mineral matter compositions to produce a slag with low T_{CV} and viscosity to achieve desired slag flow characteristics.

1.3. Objectives of the Review

For coals used in dry ash gasification processes the issues regarding mineral matter and its behaviour are very similar to the conventional pf power stations: it has to be a high AFT ash to avoid slagging or ash agglomeration, preferably with low concentration of heavy metals to minimise ash disposal problems. These issues are relatively well understood and not considered further in this review.

It is possible to divide the effects of mineral matter in coal on the slagging gasification technologies in the following groups:

- I. Issues related to the operation of the gasifier, e.g. slag flow behaviour
- II. Issues related to the reliability of gasifier, e.g. slag–refractory interactions
- III. Issues related to environmental impact, e.g. slag stability and disposal, fate of volatile elements in coal ash.

The main purpose of this review is to provide the information of the current situation in each of the three fields, to identify (where possible) major research and development ‘players’ in these areas and to recommend directions for addressing the most important issues. This review is specifically targeting coal slags in entrained flow slagging gasification and is not addressing the similar issues in other processes (such as slags in metallurgy or fly ash in conventional boilers).

2. SLAG FLOW BEHAVIOUR

2.1. Slag Flow Requirements

One of the major requirements for normal operation of a slagging gasifier is continuous and even removal of slag. To achieve that goal, the viscosity of the coal slag (according to a number of papers) should not exceed 5 Pa s for fixed bed and 25 Pa s for entrained flow slagging gasifiers [1, 3, 4, 6].

If the coal slags are too viscous at the gasifier slag tapping temperature (normally 1400–1500°C) then either an increase in gasifier operation temperature or fluxing/blending with other coals to produce less viscous slags is required. Higher operation temperatures require more coal and oxygen to be burned; consequently the efficiency of the gasifier is reduced.

The need for fluxing and/or blending also involves additional operational costs and thus affects the economics of the usage of a particular coal. In some cases, the necessity for heavy fluxing or higher operation temperatures can make a particular

coal economically unviable. Therefore slag flow properties have an important effect on fluxing and/or blending requirements and determining the minimum possible operation temperature of the gasifier. Coal slag viscosity is therefore one of the most important factors determining the suitability of a particular coal for a slagging gasification process.

To assess the suitability of a particular coal to a particular gasifier, or to optimise the fluxing and/or blending procedure, knowledge of the compositional and temperature dependence of slag flow behaviour is essential. This information could be obtained from either experimental measurements of slag flow behaviour or from estimation with predictive models of slag viscosity and T_{CV} .

The practical aspects of slag flow measurements will be discussed in the next section, followed by a review of the experimental data and modelling of slag flow behaviour available in the literature.

2.2. Experimental Techniques for Measuring Slag Flow Behaviour

Although many apparatus exist for measuring viscosities of liquids at relatively low temperatures (below $\sim 300^\circ\text{C}$), coal ash slags—which are predominantly silicate melts—are liquid at temperatures above 1000°C . At these temperatures material choice of instrument components imply strict restrictions on the instrumental design.

A brief description of the main types of viscometers suitable for measurements at high temperatures is provided below.

2.2.1. Capillary Viscometer

A schematic drawing of a capillary viscometer is given in Figure 3. A liquid drains (or is forced) through a fine-pore tube (capillary), and the viscosity is determined from the measured flow, applied pressure, and tube dimensions. The basic equation governing this process is the Hagen-Poiseuille equation:

$$\eta = \frac{\pi \cdot r^4 \cdot \Delta p \cdot t}{8 \cdot V \cdot L}$$

where η is the viscosity (Pa s), r the radius of capillary (m), Δp the pressure drop through capillary (kg/m s²), V the volume of liquid (m³) that flows in time t (s) and L the length of capillary (m).

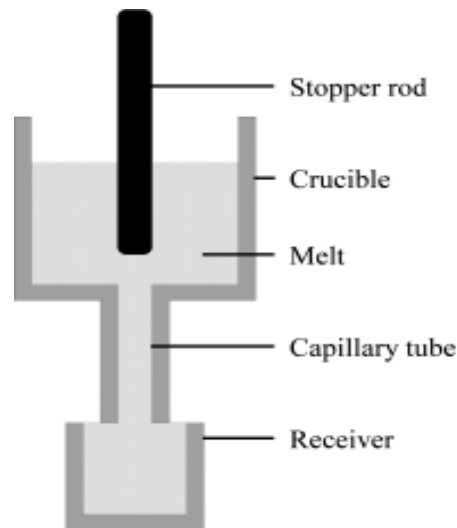


Figure 3: Schematic drawing of a capillary viscometer [7]

Capillary viscometers are one of the oldest types of viscometers. They were used in high temperature viscosity measurements for more than a century [7]. Despite their very well-developed design, they can provide inaccurate experimental data from the use of inadequate working equations.

This type of instrument is very sensitive to capillary dimensions ($\eta \propto r^4$). At temperatures above 1200°C, complications arise in the selection of a suitable crucible and capillary material in terms of dimensional stability (change of size due to the thermal expansion) and corrosion resistance [8].

2.2.2. Falling-Body Viscometer

A schematic diagram of a falling body viscometer is given in Figure 4

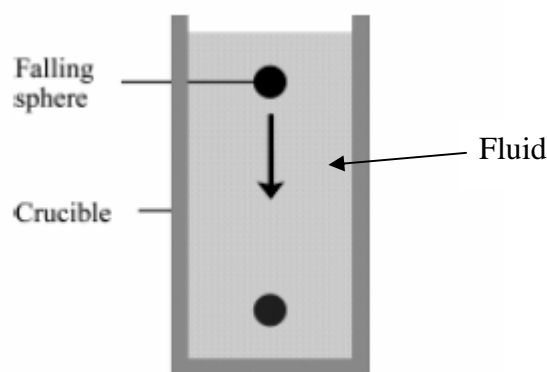


Figure 4: Schematic drawing of a falling-sphere viscometer

Viscosity is calculated on the basis of Stokes law for a sphere:

$$\eta = \frac{2r^2 g (\rho_{sphere} - \rho_{liquid})}{9v}$$

where η is the viscosity (Pa s), r the radius (m), g is the gravitational acceleration (m/s^2), ρ is the density (kg/m^3) and v is the velocity of the sphere (m/s).

The body can either fall due to gravity or it can be dragged upwards through the melt [8]. The body can also be cylindrical, and the tube in which the body falls can be inclined instead of vertical.

2.2.3. Rotational Viscometer

In a rotational viscometer, liquid is kept between two cylinders, one of which is rotated at a given speed. The viscosity is related to the torque used to maintain the rotational speed of the cylinder. Very accurate measurements are possible with rotational viscometers, providing that corrections for effects associated with the gap between rotating cylinder and crucible walls and bottom are used. Usually, the instrument is calibrated with liquids of known viscosity, but absolute determination is also possible using the Margules equation:

$$\eta = \frac{T \cdot (r_o^2 - r_i^2)}{4 \cdot \pi \cdot L \cdot \omega \cdot r_o^2 \cdot r_i^2}$$

where η is the viscosity (Pa s), T the torque (N m), r_o and r_i the radii of outer and inner cylinders (m), L the depth of penetration (m), ω the angular velocity (s^{-1}).

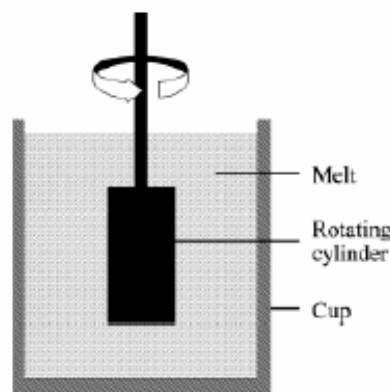


Figure 5: Schematic drawing of a rotating- cylinder viscometer [7]

Figure 5 shows a schematic drawing of a rotating-bob viscometer where the inner cylinder is rotated and the outer cup is fixed. Three variations of the geometric configurations are possible [7]:

- (i) inner cylinder rotates and outer cup is fixed
- (ii) inner cylinder is fixed and outer cup rotates
- (iii) both inner cylinder and outer cup rotate.

An evaluation of the three configurations against each other has not been found in the literature. However, the centering of the inner cylinder is of great importance in all three cases, and this may be the reason why the first configuration is most commonly used in practice.

2.2.4. Oscillation Cylinder or Plate Viscometer

In these methods the viscosity is measured by monitoring the logarithmic decrement of the swings of a pendulum oscillating in the test liquid (Figure 6).[8]

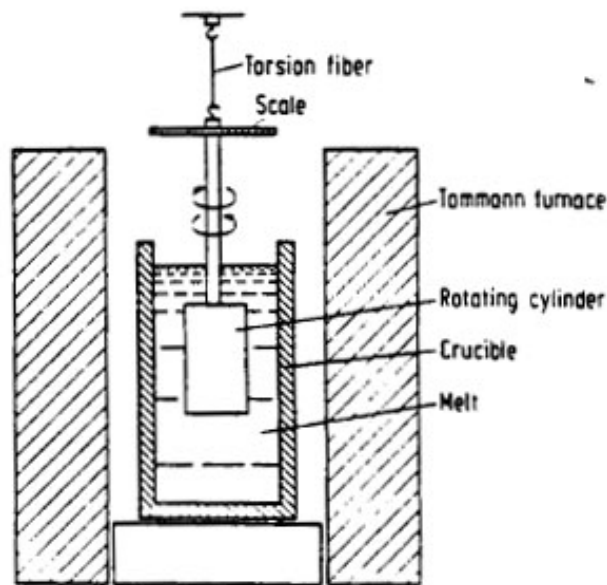


Figure 6: Schematic drawing of oscillating-cylinder method [8]

Viscosities can be calculated using the following equation:

$$\eta = \frac{2}{\pi \cdot \rho \cdot \tau} \left[\frac{2\Theta \left(\frac{\lambda}{\pi} \right) + \left(\frac{\lambda}{\pi} \right)^2 + \dots}{R^4 + R^3 \cdot d} \right]$$

where ρ is the liquid density (kg/m^3), τ is the period of oscillation in empty system (s), Θ is the moment of inertia of oscillating system (kg m^2), λ is the decrement due to damping effect of the liquid (expressed in natural logarithm), and R and d are the radius and thickness of cylinder (m).

The oscillating-plate method has been developed specially for high temperature measurements of materials with low viscosities (in the mPa s region) eg CaF_2 -based slags, metals, etc. [8]

2.2.5. Practical Aspects of High Temperature Viscometry

The viscosities of molten silicate melts varies in a range from 10^{-2} to 10^{12} Pa s, depending on their temperatures and compositions. It is essential that a viscometer chosen for the measurements of slag flow behaviour is capable of cover the viscosity range of interest.

Table 1 provides an overview of the viscosity ranges of different viscometer types.

Viscometer type	Measurement range $\log_{10} \eta$ (Pa s)
Falling-sphere viscometer	-2–6 [7]
Capillary viscometer	-2–2 [8]
Oscillating-cylinder viscometer	-3–1 [8]
Rotating-cylinder viscometer	2–13 [7]

Table 1: Measurement ranges for some viscometers.

Falling-sphere viscometers are good for material with high viscosity, however they cannot provide information in the lower viscosity range. Capillary- and oscillating-cylinder viscometers are excellent for low viscosity fluids. The only type of viscometer which covers the full desirable range is the rotational viscometer. Urbain and Boiret highlighted the superiority of the rotational viscometer over other devices for high-temperature measurements on liquid silicates [9]. Urbain et al. concluded that this method gives the best results for viscosities ranging from 1000 to 10 Pa s [10]. On the basis of the analysis of existing experimental data, Vargas et al. [7] suggested that the most accurate method for viscosity measurements at high temperatures is the rotational method.

Vargas et al. in their review [7] also considered the major properties affecting high-temperature viscosity measurements. They were:

- atmosphere
- temperature
- sample composition

The choice of atmosphere (CO:CO₂ ratio) around the sample could influence the observed viscosity, particularly for iron-containing melts. Iron will be oxidised from its ferrous (Fe²⁺) to its ferric (Fe³⁺) state when the atmosphere is changed from reducing to oxidising conditions. This change of iron oxidation state leads to increase in viscosity. While for many applications (blast furnaces, pf boilers etc) CO:CO₂ ratio is variable, under entrained flow gasification conditions it is expected that the slag is under reducing atmosphere with a relatively high CO:CO₂ ratio (15–150). Therefore, the effect of atmosphere in regards to the coal gasification issues is unlikely to be relevant. However, it is essential that the viscosity testing of coal slags for gasification purposes be conducted in a reduced or, at least, neutral environment with negligible amounts of oxygen (very high CO:CO₂ ratio).

During experimental determination of slag viscosity, the composition of the sample can change during heat-up due to the selective evaporation of some slag components. It is therefore essential to verify the composition of the slag by analysing it after the test. Furthermore, to minimise the effects of selective evaporation losses, it is recommended that the measurements be conducted from high temperatures downwards.

Another factor affecting the composition of the measured slags is an interaction of slag with the crucible and sensor (e.g. rotating bob) material. In a study on low-rank coal slags, Streeter et al.[11] initially melted the slag in crucibles of vitreous carbon. As a result of the reduction of slag by the carbon, small pools of molten iron settled from the slag. When the carbon crucibles were replaced with high-purity alumina crucibles, metallic iron was rarely observed in the slag. However, varying degrees of attack on the alumina crucible by the slag were observed. Generally, dissolution of Al₂O₃ by the slag was slight, but occasionally a noticeable thinning of the crucible walls did occur [11]. The contamination of coal ash slags by alumina crucibles usually is in the order of few weight percent in acid slags, but in basic slags can be much higher (10–15%)[7]. Particularly corrosive are the low-rank coal slags.

Platinum could be used as a crucible and sensor material to avoid contamination of the test slag [7], but not for iron-containing slags in reducing atmospheres [12]. The reactions between iron contained in the slag and metallic platinum under a reducing environment make platinum crucibles or sensors unsuitable for slag studies for coal gasification.

Only those of the studies of silicate melt viscosities which employ molybdenum or tungsten sensors should be regarded as trustworthy [7]. The use of molybdenum

and/or tungsten components resulted in negligible contamination of tested material (10–20 ppm w/w) [13]. Molybdenum and tungsten are ideal materials for studies of slag flow behaviour under gasification conditions, since they are stable at high temperatures under non-oxidising environments.

To allow further assessment of experimental data, Vargas et al. [7] recommended providing the following information when publishing any experimental data:

- description of experimental apparatus, including sensor material and dimensions
- reproducibility data, including accuracy and precision data and information on how this was obtained
- comprehensive description of test procedures including the pre-treatment of the test material
- composition of test atmosphere
- slag composition as measured after the test-run including information on analytical technique used
- iron oxidation state
- tabulated measurement data.

2.3. Effects of Composition on Slag Flow Behaviour

Since slag composition is the most important factor affecting slag flow behaviour at a given temperature, there have been extensive studies in this area. The compositional effects on silicate melt viscosity are not understood in detail; however it appears that the network theory suffices to explain many aspects of viscosity behaviour. It assumes that the individual oxides could be grouped according to their effect on the silica network. Some oxides appear to act as either network formers (increasing the viscosity) or modifiers (decreasing the slag viscosity); others seem to play less clearly defined roles.

Silicon dioxide (SiO_2) is the dominant network former, and the addition of most of the other oxides to SiO_2 will usually lead to a decrease in viscosity. The alkali oxides (Na_2O , K_2O , Li_2O) can all be classified as network modifiers. The alkaline earth oxides (e.g. MgO , CaO) play more complex structural roles depending on the overall composition of the melt, although they mostly act as network modifiers, reducing the slag viscosity. At high concentrations of Ca and Mg, the slag viscosity response to temperature changes becomes much sharper and sometimes results in increase of T_{CV} .

Aluminium oxide can act as both network former or as a network modifier, depending on the slag chemistry. If the negative charge of the aluminium in tetrahedral position is compensated by available alkali or alkali-earth elements, it acts

as a network former, increasing the slag viscosity. If the presence of alkali or alkali-earth elements is insufficient to compensate the negative charge, aluminium acts as a network modifier, decreasing slag viscosity.

Effects of ferric iron oxide (Fe_2O_3) are similar to that of aluminium, whereas ferrous iron oxide (FeO) acts as network modifier. The structural role of titanium oxide in silicate melts is not well understood, however it seems to show amphoteric behaviour, depending on the composition of the slag.

A large number of measurements of rheological properties of silicate melts are reported in the literature. However most of them are related to either metallurgical slags or glass production. The purpose of the current paper is to give an insight on the situation with coal slags in particular.

Australian coal slags could be approximated as quaternary systems of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-FeO}_x$ with small amounts of MgO (~0.1–4%), Na_2O (~0.1–2.3%), K_2O (~0.1–4%) and TiO_2 (typically 0.6–3%). The silicate melts relevant to metallurgical technologies usually have higher concentrations of other oxides, such as TiO_2 , CuO , Cr_2O_3 , ZnO , PbO . Silicate melts in glass production typically have high concentrations of alkali oxides (Na_2O , K_2O , Li_2O) and B_2O_3 .

Table 2 provides an overview of major research in the slag flow behaviour of coal slags related to gasification technologies.

Authors	Group	Compositional Range					Atm.	Comments
		SiO_2	Al_2O_3	CaO	Fe	MgO		
Quon et al.	CANMET	61–69	18–22	2–6	3–5 as Fe_2O_3		Ox	Western Canadian bituminous coals [14, 15]
Quon et al.	CANMET	42–45	22–25	14	5–6 as Fe_2O_3		Ox	Western Canadian lignites [14, 15]
Chen et al. Vorres et al.	Argonne National Laboratory	30–50	5–25	10–30	5–25 as FeO	0–20	Red, Neut, Ox	Synthetic and natural coal slags [16]
Rhine and Mills	NPL	27–37	11–30	10–35	1–12 as Fe	1–5	Red	Real slags [17, 68]
Hurst and Patterson	CSIRO/CCSD	20–70	4–50	0–40	0–33 as Fe_2O_3	0–10	Red, Neut	Synthetic and natural coal slags [2-4, 19-24]
Hurley et al.	University of North Dakota	39	21	23	23 as Fe_2O_3		Red, Air, Air+ H_2O	Powder River Basin coal [25-27]

Table 2: Major studies of the compositional effects of slag viscosity of coal ash slags related to gasification technologies. Ox = oxidising, Red = reducing, Neut = neutral.

Quon et al. [14, 15] studied viscosities of slags from Western Canadian bituminous coals and lignites under oxidising conditions. It was shown that viscosities are inversely proportional to $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ mass ratios and the base/acid ratio of the slags. For example, at 1500°C an increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 2.3 to 3.3 results in drop of viscosity from 25 to 3 Pa s. Similarly, at the same temperature, an increase in the base/acid ratio from 0.1 to 0.4 results in viscosity decrease from 20 to 1.5 Pa s respectively.

These findings were confirmed by Chen et al. [16] and Vorres et al. [28]. This team from Argonne National Laboratory studied effects of composition, temperature and atmosphere on viscosities of synthetic and natural coal slags. The slags with greatest SiO_2 content had highest viscosity. For a given SiO_2 content, the slags with highest Al_2O_3 content had the highest viscosity. Therefore, silica to alumina ratio (S/A) was found to be an important parameter affecting slag viscosity.

Rhine and Mills [17, 18] showed that the viscosity of any given slag composition is a function of temperature and oxygen partial pressure. Oxygen partial pressures in these experiments were either typical of slagging-coal-gasifier conditions (P_{O_2} between 10^{-8} and 10^{-9} atm) or, in some cases, an ambient air environment. As expected, the sensitivity of slag flow behaviour to oxygen partial pressure was greatest for slags with high Fe content. Both T_{CV} and viscosities of slags with high iron content (25 wt%) were much higher in air compared to the ones measured under a reduced atmosphere. Flow behaviour of slags with low (<5 %wt) iron content was insensitive to oxygen partial pressure.

Hurley et al. studied the effects of atmosphere on slag viscosity from both slag flow behaviour and refractory corrosion perspectives [25-27]. They measured viscosities and T_{CV} of Powder River Basin coal slag in three atmospheres: air, air and 10% water vapour, and reducing atmosphere [25, 26]. They found that reducing atmosphere reduces slag viscosity. The T_{CV} (the temperature below which the viscosity increases dramatically) was approximately 1250°C in air and air + water vapour, but dropped to 1180°C when measured in a reducing atmosphere [25, 26].

The effect of oxygen partial pressure on slag flow behaviour was explained as the effect of $\text{Fe}^{3+}/\text{Fe}^{2+}$ equilibrium in slags [27]. The lower values of slag viscosities measured under reducing conditions are assigned to the transformation of network-forming ferric iron to the network-modifying ferrous iron. The T_{CV} is associated with a eutectic temperature in the phase diagram for the closest ternary system. Again, the higher iron content in slag, the stronger slag flow dependence on oxygen partial pressure.

The most comprehensive and systematic experimental studies of compositional dependence of coal slag flow behaviour have been conducted as a major research

program for Australian coals by CSIRO and CCSD. Within this program the slag flow behaviour for a wide range of Australian coal slag compositions was measured and these data used as the basis of an assessment of coals for use in entrained-flow gasification.

These experiments resulted in a unique database of coal slag flow measurements performed under consistent, well-defined conditions. It consists of viscosity vs temperature measurements of more than 270 slags made from real coal ash, and 80 synthetic slags. This dataset covers almost all important compositions of Australian coals (Figure 7).

These results have been reported by Hurst and Patterson [2-4, 19-24] and Kinaev[29]. These data have been used for the development and testing of viscosity models by a number of different authors [19, 20, 30-35]. The data have also been used as the basis of a comprehensive survey of the suitability of Australian coals for gasification applications from the slagging point of view [36].

These experimental studies provided data on slag flow dependence on such compositional characteristics as S/A, CaO and iron content in coal slag. The effects of magnesia and sodium content in coal slag were not studied, since the variations of Mg and Na in Australian coals are not considered significant.

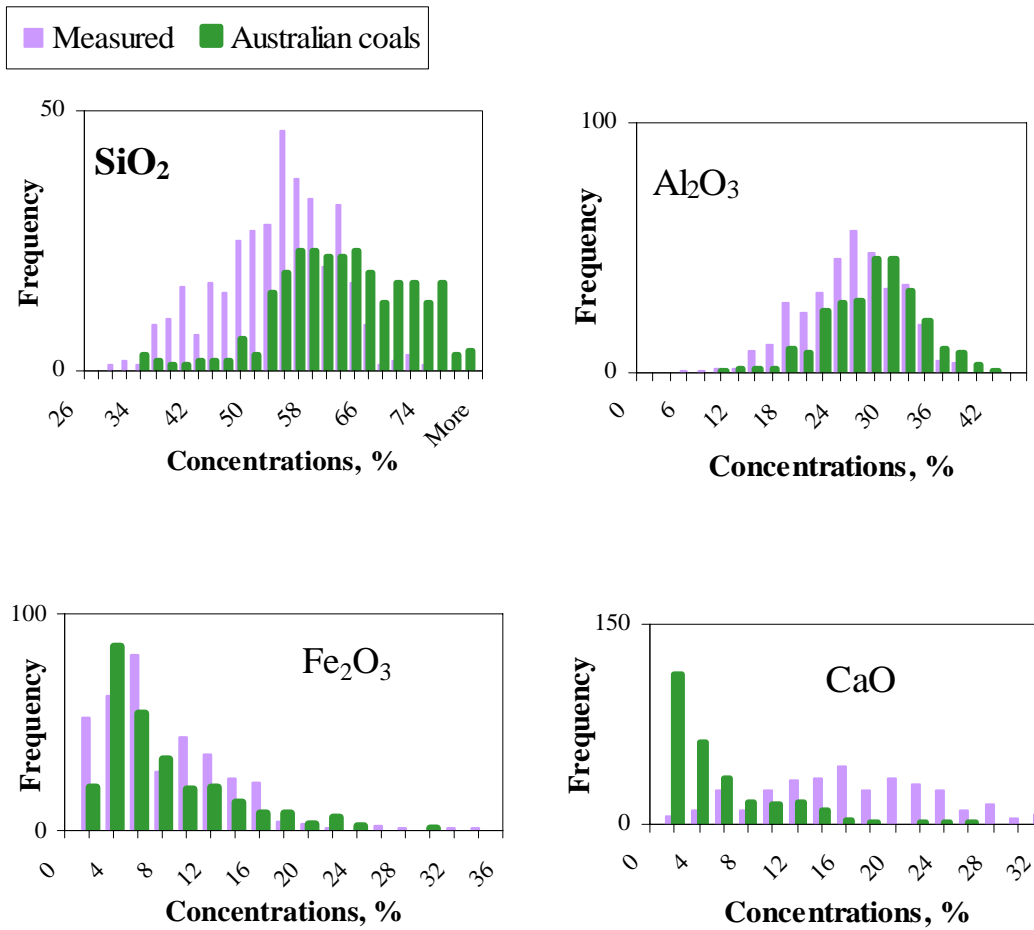


Figure 7: Range of concentrations of major components of measured coal slags (purple) and typical Australian coals (green).

Iron content was used to group the ranges of composition-based data. For each compositional group of slags the coal gasification suitability maps in S/A–CaO coordinates were developed. Examples of such maps are given in Figure 8 and Figure 9. The green areas correspond to the optimum compositional ranges (i.e. slag viscosities at 1400°C are between 5 and 25 Pa s). The yellow areas correspond to the compositional ranges where slag flow characteristics are on the edge of suitability: viscosities are either too low (2–5 Pa s) or too high (25–50 Pa s). Red area indicates T_{CV}-precluded zones, where slags are not flowing because of the high amount of crystallised solids. The compositional range studied covers almost all important Australian thermal coals.

The completion of this program allows optimisation of fluxing and/or blending of Australian coals to suite particular slagging gasification processes.

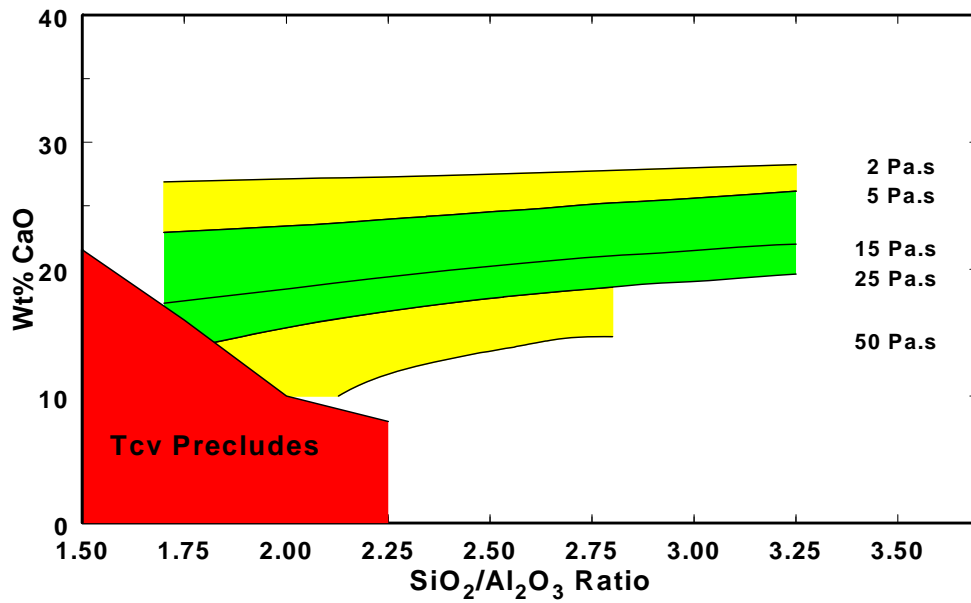


Figure 8: Suitability of coal slags containing 5 wt% FeO [37].

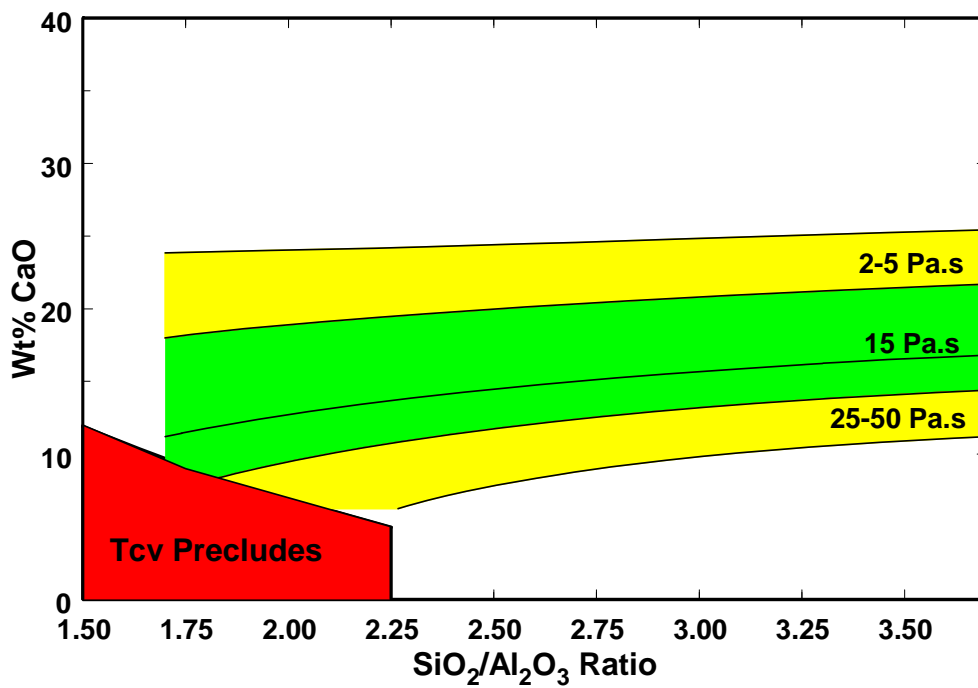


Figure 9: Suitability of coal slags containing 10 wt% FeO [37].

2.4. Effects of Heterogeneities on Slag Flow Behaviour

There is a very limited number of studies on the effects of heterogeneities in slags on flow behaviour available in the literature. This paucity of data is most likely due to limited availability of well understood slag samples with real heterogeneities and difficulties in design of such type of experiments, which requires fast quenching of relatively large slag samples (100–200 grams).

During cooling of slag, partial crystallisation of different phases is possible. The most common phases in the coal ash slags are spinels, mullite, anorthite, and hematite group, including corundum.

Spinel is a group of oxides that have very similar structures, containing over twenty members. The general formula of the spinel group is AB_2O_4 . The **A** represents a divalent metal ion such as magnesium, iron, nickel, manganese or zinc. The tetravalent lead ion can also occupy this site. The **B** represents trivalent metal ions such as aluminium, iron, chromium or manganese; titanium may also occupy this site with a +4 charge and lead at +2 can occupy this site. The formation of solid solutions is common in this group of minerals, meaning that they may contain certain percentages of different ions in any particular specimen.

Anorthite is a member of the so-called plagioclase series. This series includes minerals that range in chemical composition from pure $NaAlSi_3O_8$ (albite) to pure $CaAl_2Si_2O_8$ (anorthite). Anorthite by definition contains no more than 10% sodium and no less than 90% calcium in the sodium/calcium position in the crystal structure.

Mullite is the mineralogical name given to the only chemically stable intermediate phase in the SiO_2 – Al_2O_3 system. It is commonly denoted as $3Al_2O_3 \cdot 2SiO_2$ (i.e. 60 mol% Al_2O_3). However it is actually a solid solution with the equilibrium composition limits of 60–63mol% Al_2O_3 below 1600°C.

The hematite group is a group of closely related trigonal oxides with similar structures. The general formula for this group is A_2O_3 . The **A** cations can be iron (hematite), titanium, aluminium (corundum), chromium, vanadium, magnesium, antimony, sodium, zinc or manganese. The structure is composed of alternating layers of cations and oxygen ions. The cations occupy spaces in layers between the layers of oxygen ions and each are bonded to three oxygen ions in the above layer and three oxygen ions in the bottom layer. Not all of the sites for these cations are occupied as only two out of three are filled. If all the sites were filled then the formula would be **AO** instead of A_2O_3 .

Oh et al. studied the effect of crystalline phase formed on coal slag viscosity [38, 39]. It was found that an extensive network formation of dendrite-shaped spinels

caused a rapid increase in the viscosity, while anorthites and large spinels and elongated particles of corundum did not affect the slag viscosity as much.

Another attempt to connect the slag flow behaviour with crystalline phases available in the slag has been done by Kinaev [29]. In this work, the connection between slag phase composition and T_{CV} was established. For slags where the crystallising solid phase is mullite, the T_{CV} occurs at the temperature at which the content of solid phase is between 17 to 20wt%. A small amount of crystallised corundum does not change the critical amount of solids. However, increasing the amount of corundum in the solid phase decreases the amount of solids required to achieve T_{CV} from 20 to 14wt%. When one of the crystallising phases is spinel, the critical amount of solids is lowered to within the range 14–9wt%. The lowest critical amount of solids is observed when there is a multiphase combination of solids, including spinel, crystallising in the slag.

Therefore it is important to be able to predict the amount and type of crystalline phase formation under a given experimental condition, since this slag phase composition has a direct link with slag flow behaviour. Phase composition predictions require a thermodynamic equilibrium analysis as well as studies of kinetics of phase formation as a function of temperature.

Gas bubbles of carbon monoxide and metallic iron, both produced as a result of reduction of iron oxides in slag by graphite crucible (where used), also lead to a decrease in observed viscosities [17]. However, reported data is not conclusive and it is not clear whether this is solely an effect of heterogeneities or a consequence of transforming iron from network former to network modifier by reducing ferric to ferrous oxide.

Examination of real gasifier slags [40] showed that they can contain heterogeneities such as gas bubbles, metallic iron and ‘marbling’ (uneven chemical composition of the slag), as viewed under SEM. No crystals at sub-liquidus temperatures were reported, as opposed to the laboratory viscosity measurements. No quantification of the possible effects on slag flow behaviour was presented.

Thus, both the relevance of different heterogeneities (other than crystalline phases) and their quantitative effects on slag flow behaviour remain unclear.

2.5. Modelling Slag Viscosity

The situation with respect to the modelling of silicate melt viscosity is quite complicated. On one hand there are quite a number of empirical or semi-empirical predictions of slag viscosities for certain compositional ranges [2, 7, 9, 19-23, 30-32, 35, 37, 39-41, 56-67]; on the other hand some work has been done in theoretical understanding of the viscosity of glass forming liquids without yet resulting in a

practical workable model [43-54]. In the slag viscosity literature, all of these are called ‘models’. To avoid confusion in the discussion of these, the following terms will be used throughout this review:

- ‘Model’ refers to a theoretical model, based on first principles, preferably with no (or a minimum amount of) fitting parameters. Such a model explains the nature of slag flow behaviour and it should be valid over a wide compositional range.
- ‘Semi-empirical model’ is a correlation based on a theoretical equation, with a reasonable amount of fitting parameters. The main purpose of semi-empirical models is to predict slag flow behaviour within a relatively wide compositional range.
- ‘Empirical correlation’ is a correlation of experimental data with fitting parameters, designed to predict slag flow behaviour over a narrow, specific compositional range.

Vargas et al. [7] conducted a test of the performance of empirical correlations and semi-empirical models of silicate slags with a SiO₂ concentration of between 20 and 75mol%. It was found that the tested models were capable of predicting viscosity only within several orders of magnitude of the reported measurements. They were tested only for six different viscosity vs temperature datasets using mixtures of varying compositions. For some compositions all the models performed well, and for others they did not. It was suggested that the valid way to select a model is to choose one that performs well on slags of similar compositions as the one required.

All the semi-empirical models considered by Vargas et al. are based on the network theory; however they depend largely on experimental observations of varying reliability. It therefore seems that to introduce major improvements to performance of slag viscosity predictions, a more fundamental understanding of the compositional effects on slag flow behaviour is required.

All empirical correlations and semi-empirical models reviewed by Vargas et al. were designed for the prediction of the viscosity of completely molten samples. If a studied slag contains some solids, it will most likely not exhibit Newtonian behaviour, and viscosity determination will have to depend either fully or partially on experimental procedures. If the crystal fraction and shape are known, there are some simple models that can give an indication of the overall viscosity of the mixture. These models for heterogeneous slags will also be considered in later sections.

2.5.1. Models for Homogeneous Slags

On a molecular level, viscous flow of a fully liquid slag involves relative movements of the structural elements of the liquid. The probability of such a displacement to

occur is a product of the probability that an empty space is available in front of the structural unit and a probability that the energy of the structural unit is enough to move to the empty space. The differences between models of slag viscosity are only in their descriptions of those probabilities as a function of slag composition.

A brief summary of the viscosity models of homogeneous slag is provided Table 3.

Theoretical basis	Model	Advantages	Limitations	Authors
Arrhenius	S ²	Simple to use	Limited composition range, tends to underestimate viscosities	Reid-Cohen [7]
	Watt-Fereday	Simple to use	Overestimate viscosities, limited composition range	Watt-Fereday [55]
	Shaw	Relatively simple to use	No physical justification, underestimates viscosities, limited compositional range	Shaw [7]
Frenkel-Weymann	Urbain and Modified Urbain	Larger compositional range	Harder to use. Still high discrepancies between predictions and experimental results	Urbain [56], Boiret [9, 57] Kondratiev, Jak [32, 33, 41]
	Kalmanovitch - Frank	Larger compositional range	Harder to use. Still high discrepancies between predictions and experimental results	Kalmanovitch – Frank [58]
	Riboud	Larger compositional range, easy to use	Inaccurate viscosity predictions over some composition ranges	Riboud [59]
	Structural model	Large compositional range	Hard to use. Requires thermodynamic packages. Tends to underestimate viscosities	Zhang, Jhanshahi [60-66]
Eyring	UQ “quasi-chemical”	Large compositional range	Hard to use, excessively big amount of fitting parameters. Requires thermodynamic packages. Tends to underestimate viscosities	Kondratiev, Jak [32, 33, 41,42]
Empirical correlation	CSIRO/CCSD	Simple to use	Very limited compositional ranges, poor predictions on the boundaries	Hurst, Browning Patterson[21, 30, 31, 67]

Table 3: Major viscosity models for homogeneous coal slags

2.5.1.1. Arrhenius-Type Correlations

The most simple group of models is based on the Arrhenius-type equation

$$\eta = A \cdot e^{\frac{E_a}{T}}$$

where T is temperature and A and E_a are essentially composition-dependent constants: in this equation A represents the probability of an empty space before the structural unit and E_a is an activation energy required to jump into this space.

Several models belong to this group. The S^2 model [7] uses a modified Arrhenius equation:

$$\eta = 4.468 \left(\frac{\zeta}{100} \right)^2 e^{\frac{1.265 \cdot 10^4}{T} - 8.44}$$

where silica ratio ζ is calculated on a weight basis:

$$\zeta = \frac{100 \cdot SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO}$$

This model implies that the probability coefficient depends on the silica ratio, and activation energy is compositionally independent. As a result, this model is valid only for a limited compositional range.

The Watt-Fereday model [55] also uses Arrhenius-type equation:

$$\eta = A \cdot e^{\frac{E_a \cdot 10^7}{(T-423)^2}}$$

where activation energy is presented as a first degree polynomial of silica and alumina composition-derived parameter:

$$E_a = 0.00835 SiO_2 + 0.000601 Al_2O_3 - 0.109$$

and the probability of formation of ‘free volume’ is a first degree polynomial of all four major oxides:

$$A = 0.0415 SiO_2 + 0.0192 Al_2O_3 + 0.0276 Fe_2O_3 + 0.0160 CaO - 4.92$$

This model includes sets of individual parameters for each oxide. Again, this model is applied to a limited compositional range and generally overestimates the viscosities of multi-component slags.

The model developed by Shaw [7] uses a modified Arrhenius equation:

$$\eta = \frac{C\eta}{C_T\alpha} \cdot e^{\frac{\alpha 10^4}{T}}$$

Here, both the probability coefficient and activation energy depend on the same composition-derived parameter α . This parameter is calculated using the equation:

$$\alpha = \frac{x_{SiO_2} \cdot \sum x_i \cdot \alpha_i^0}{1 - x_{SiO_2}}$$

where x_i represents the molar fraction of oxides (SiO₂, K₂O, Na₂O, Li₂O, MgO, FeO, CaO, TiO₂ and 'AlO₂') in the slag and α_i^0 is an individual parameters for each oxide. This particular connection between E_a and A has no physical justification and based solely on the empirical data. Shaw's model is also applicable for a limited compositional range and usually underestimates viscosities.

2.5.1.2. Frenkel-Weymann Equation

Quite a number of semi-empirical models described in the literature are based on the Frenkel-Weymann equation

$$\eta = A \cdot T \cdot e^{\frac{E_a}{T}}$$

The most common of these is Urbain's model [56], where all species in the melt are grouped as network formers, network modifiers or as amphoteric:

$$x_g = SiO_2 + P_2O_5$$

$$x_m = FeO + CaO + MgO + Na_2O + K_2O + MnO + NiO + 2(TiO_2 + ZrO_2) + 3CaF_2$$

$$x_a = Al_2O_3 + Fe_2O_3 + B_2O_3$$

Then a parameter α is calculated as

$$\alpha = \frac{x_m}{x_m + x_a}$$

In the next step parameter b (related to activation energy as $E_a = b \cdot 10^3$) can be calculated by combination of four parabolic equations using α and the molar ratio of silica SiO₂.

$$b_0 = 13.8 + 39.9355 \alpha - 44.049 \alpha^2$$

$$b_1 = 30.481 - 117.1505 \alpha + 129.9978 \alpha^2$$

$$b_2 = 240.9429 + 234.0486 \alpha - 300.04 \alpha^2$$

$$b_3 = 60.7619 - 153.927 \alpha + 211.1616 \alpha^2$$

$$b = b_0 + b_1 \text{SiO}_2 + b_2 \text{SiO}_2^2 + b_3 \text{SiO}_2^3$$

Parameters A and b are related by the equation

$$\ln A = m \cdot b + n$$

where m and n are also empirical parameters. Initially Urbain suggested universal values of parameters m and n as 0.2693 and 13.9751 respectively [56]. However, in the modified Urbain model [9, 57] it was suggested that different sets of m and n be used for different types of melts. Overall this model is applicable to a wider compositional range compared to Arrhenius-based models, and predicts viscosities to within an order of magnitude. Often the calculated values differ from the experimental viscosities by less than a factor of two.

The Kalmanovitch–Frank model [58] differs from Urbain model only by different values of parameters m and n in the same equation

$$\ln A = m \cdot b + n$$

This model shows the same reasonable agreement with experimental data as the Urbain model and has no clear advantages over it [7].

The Riboud model [59] approximates parameters A and b in Frenkel-Weynman equation using a first degree polynomial of molar concentrations of slag component:

$$\ln A = 235.76 \text{Al}_2\text{O}_3 + 1.73 (\text{FeO} + \text{CaO} + \text{MgO} + \text{MnO}) + 7.02 (\text{Na}_2\text{O} + \text{K}_2\text{O}) + 5.82 \text{CaF}_2 - 1.81$$

$$b = 68.833 \text{Al}_2\text{O}_3 - 23.896 (\text{FeO} + \text{CaO} + \text{MgO} + \text{MnO}) - 39.159 (\text{Na}_2\text{O} + \text{K}_2\text{O}) - 46.356 \text{CaF}_2 + 31.140$$

Mills [68] found that in calculation of viscosities of gasification slags it is marginally less-successful than the Urbain model.

Another approach is to use so-called ‘structural model’ developed by CSIRO [60-66]. In this semi-empirical model an activation energy parameter, E_a , for a binary oxide system is expressed as a function of fraction of bridging and free oxygen in the melt by the equation:

$$E_a = a + b(N_{O^0})^3 + c(N_{O^0})^2 + d(N_{O^{2-}})$$

where N_{O^0} and $N_{O^{2-}}$ are fractions of bridging and free oxygen respectively and a , b , c and d are fitting parameters which have been optimised against experimental data. The fraction of bridging and free oxygen in the melts has to be determined by usage of the one of the existing thermodynamic databases (e.g. MPE, FactSage etc).

Then, as in Urbain's model, the probability parameter A is calculated using the equation:

$$\ln A = a_i + b_i E_a$$

where a_i and b_i are fitting parameters optimised for this binary system.

This semi-empirical model assumes that for higher-order (ternary, quaternary etc.) silicate systems each of the fitting parameters a , b , c , d , a_i and b_i is a linear function of those in binary systems. It means that they can be represented as

$$a = \sum_{j=1}^m X_j a_j, \quad b = \sum_{j=1}^m X_j b_j, \quad c = \sum_{j=1}^m X_j c_j \quad \text{etc.}$$

where m is the number of non-silica components in the system, j is the j^{th} non-silica component and X_j is its normalised mole fraction.

This semi-empirical model cannot predict viscosity from first principles or from other easily-measured macro-characteristics of the melt (e.g. heat capacity or thermal conductivity). It provides reasonable performance over a wide range of slag compositions. However it has a tendency to overestimate viscosities for slags with medium and high iron content ($\text{FeO} > 5\%$) in the viscosity range between 10 and 50 Pa s.

Kondratiev and Jak[32, 33, 41] also introduced a number of modifications into the Eyring equation. This equation is similar to Frenkel-Weynman equation and also based on the concept of "a thermally activated kinetic process in which atom or molecule in simple liquids goes from one equilibrium position to another jumping over a potential barrier"[42] :

$$\eta = \frac{2RT(2\pi k m_{su} T)^{1/2}}{\Delta E_v v_{su}^{2/3}} e^{\frac{E_a}{RT}}$$

where R is the gas constant (J/K/mol), k is the Boltzman constant (J/K), T is the absolute temperature, ΔE_v is the energy of vaporization (J/mol), E_a is the activation energy (J/mol) and m_{su} and v_{su} are the weight and the volume of structural unit..

In this modification of the model, mass and volume of structural units is estimated as:

$$m_{su} = \sum_i m_{su,i} \cdot X_i \quad \text{and} \quad v_{su} = \sum_i v_{su,i} \cdot X_i$$

where X_i , $m_{su,i}$ and $v_{su,i}$ are molar fraction, mass and volume of i^{th} structural unit respectively.

Then, similar to the ‘structural model’, Kondratiev and Jak [42] suggest replacing oxide concentrations with the concentrations of structural units, such as Si-O-Si, Si-O-Me and Me-O-Me (where Me could be Fe, Al, Ca, Na, K etc, depending on the slag composition). Concentrations of these structural units are calculated using thermodynamic software/database package “FactSage”. Parameter E_a in the Eyring equation is presented as a polynomial approximation of individual activation energies for structural units combined with the composition dependant ‘charge compensation member’:

$$E_a = \sum_i E_{a,i} \cdot X_i + B(X_j)$$

where X_i and $E_{a,i}$ are molar fraction and a ‘molar activation energy’ of i^{th} structural unit respectively, and $B(X_j)$ is the ‘charge compensation member’ (this is a function of molar fractions of $Me-j$ structural units, where Me is Al, Ca, Fe and Mg, and j is Si, Ca, Al and Mg). This ‘charge compensation member’ is described in detail in the original publication [41]. $E_{a,i}$ are in turn calculated as polynomial approximations of molar fractions of the structural units, producing a complicated set of equations with more than 30 fitting parameters for the 5-component system (Al₂O₃–CaO–‘FeO’–MgO–SiO₂).

Vaporisation energy of an ‘average structural unit’ ΔE_v is presented as an exponential product of fitting parameters for individual structural units:

$$\Delta E_v = e^{\sum_i \varepsilon_{v,i} X_i}$$

where $\varepsilon_{v,i}$ is so-called “dimensionless partial vaporisation energy” of i^{th} type of structural unit.

In this model, $\varepsilon_{v,i}$ are presented as either fitting parameters (for some of the structural units) optimised over wide dataset, or as a polynomial approximation of molar fraction of structural units (for several structural units).

Although these polynomial expressions do not have a direct physical meaning, these models provide reasonable predictability of slag flow characteristics of a large range of compositions and temperatures. However these models have a large number of

fitting parameters, which have to be re-determined if any new components are added to the system (eg K_2O , MgO , Na_2O etc). Another disadvantage is that in the practically important viscosity range for gasification systems (10–50 Pa s) this model has a trend of underestimating viscosities, sometimes by a factor of two.

2.5.2. Models for Heterogeneous Slags

The problem of taking into account the presence of crystal phases in the slag melt was partially overcome by Kondratiev and Jak [41]. They presented viscosity models of partly-crystallised slag in the $SiO_2-Al_2O_3-CaO-FeO$ system. Their models were developed in combination with thermodynamic computer packages (F*A*C*T [41]). The role of these packages is to predict the amount of solids precipitated out of the liquid slag phase and the composition of the remaining liquid phase.

The Roscoe equation with new empirical parameters provides reasonable agreement with experimental data for heterogeneous slags:

$$\eta = \eta_0 (1 - af)^n$$

where η and η_0 , where η is the overall viscosity, i.e. the viscosity of a (solid phase/liquid slag) mixture and η_0 is the viscosity of the remaining liquid phase, f is the volume fraction of the solids in the melt, and a and n are fitting parameters, which depends on the particle shape and temperature.

2.6. Summary of Studies on Slag Flow Behaviour

The situation with regards to measurements of coal slag flow behaviour is as follows:

- A database of the slag flow behaviour of slags with compositions corresponding to the majority of Australian coals exists, and coals suitable for gasification from this point of view can be identified.
- There are no reliable tools to predict T_{CV} , however preliminary findings indicate that T_{CV} could be predicted through the knowledge of slag phase composition.
- The effect of $CO:CO_2$ ratio on the viscosity of coal slags has not yet been systematically measured, but it is unlikely to be a significant issue in coal gasification.
- There are no systematic experimental measurements on the effects of heterogeneities (gas bubbles, carbon and refractory particles etc.) on the slag flow behaviour; but again, it does not appear to be a high priority issue.

The literature provides very few indications of the scale of influence of non-slag heterogeneities (e.g. gas bubbles, carbon and refractory particles) on slag flow behaviour. Therefore, before proceeding to any substantial experimental program on studies of these effects, a limited number of experiments should be done to experimentally evaluate the significance of this issue.

The more important issue is the ability to predict T_{CV} on the basis of the phase composition and phase morphology of the molten slag. Preliminary pursuing this avenue does not require any substantial additional experimental work and could be done through the analysis of the available experimental data combined with the thermodynamic predictions of the slag composition. Success in this area would provide, for the first time, the ability to predict temperatures at which otherwise suitably-viscous coal slags could not be successfully tapped in entrained flow gasifiers due to the onset of T_{CV} .

The predictability of a variety of ‘models’ remains unclear. Several estimations of the models’ performance have been reported over very limited compositional ranges. No comprehensive comparison of the performance of different viscosity models for the predictions of the behaviour of real slags, under practical gasification conditions, over the whole composition range of Australian coals is reported in the literature so far.

Despite the availability of a number of empirical viscosity models providing reasonable slag flow predictions over specific temperature–composition ranges, a solid scientific model, explaining the viscosity behaviour for the whole temperature–compositional range of silicate melts, is still lacking. Whilst such theoretical understanding and modelling of slag flow behaviour is not likely to provide a fast practical outcome, it is still seen as necessary to improve slag flow predictions on the whole slag compositions for both Australian and overseas coals.

2.7. Slag Flow Behaviour: Conclusions and Recommendations

Most of the information required for coal selection for gasification (from the slag flow point of view) is available for a wide range of Australian coals. Such data allow recommendations for coal fluxing/blending options to be made by both coal exporters and gasifier operators relevant for a range of gasification technologies.

Existing slag flow predictive models need to be integrated into industry-oriented coal evaluation tools. Before this is undertaken, however, they require an assessment of their performance for real slags. There is currently an opportunity to provide a ‘round robin’ exercise to validate existing empirical models on the basis of the extensive experimental database developed by the CCSD. It requires a comparison of available experimental results (for 20–30 different coal compositions, covering the major

Australian coals) with the calculations performed by different models. Such a comparison would clearly indicate any necessity for further work in improving the empirical models, and also to choose the most suitable model for use on Australian coals in IGCC systems.

Existing experimental data on slag flow behaviour should also be used to work towards predictions of T_{CV} for different coals. The connection between phase composition and T_{CV} has a potential to allow T_{CV} to be predicted.

The other important avenue for the further work relates to the fact that real gasifier slags contains significant amount of heterogeneous inclusions. Since the effect of these inclusions on the slag viscosity is not readily determined by current laboratory setup, it is desirable to relate the laboratory testing of slag flow behaviour to the real operations of the gasifiers through establishing closer links with the existing gasifiers operators.

3. SLAG–REFRACTORY INTERACTIONS

The gasification chamber of an entrained-flow gasifier typically operates at temperatures up to, and probably over, 1800°C, and at pressures of 20 bar or higher. The steel walls of this chamber are either water cooled or lined with refractory materials to contain the process and to protect the vessel shell from erosion, corrosion, and high temperature. At these extreme conditions, the liquid slag can corrode and react with the refractory liner, significantly limiting refractory service life and gasifier operation.

Two types of walls are used in entrained-flow gasifier design: water cooled and air cooled. Water cooled gasifiers could be of two types : with metal water cooled wall (eg. Shell, Prenflo) and with a working face lining of Al₂O₃–SiC refractory. This results in a good service life because slag solidifies on the refractory surface, forming protective layer, which decreases slag penetration and corrosion. Air cooled walls have lower service life but better thermal insulation; energy losses of the gasification chamber are less. The long refractory service life of the water cooled design is partly offset by a slight reduction in efficiency compared with the air cooled design.

Despite the fact that air cooled entrained-flow gasifiers are lined with refractory materials designed to provide the best service life and thermal insulation performance, refractory liners survive anywhere from three months to two and a half years. Gasifier operators and designers using air cooled systems have identified refractory service life as the most important factor limiting their on-line availability [70, 71].

The following aspects of slag–refractory interactions issues are reviewed:

- I. Relevance of the issue to the industry
- II. Mechanisms of slag-refractory interactions
- III. Existing testing procedures

3.1. Industrial Relevance

According to the review by Collot [1], the service time for refractory materials in slagging gasifiers is less than two years. This agrees well with the operational information from Eastman Chemicals presented by Mook [72]. In the Eastman gasification reliability model, the average life of the refractory gasifier liner is estimated at 12,000 hours (500 days) and changeover time is 22 days. It is expected that during operation of the gasifier the refractory change (even when planned) would require on average 15 to 30 days per year.

Refractory replacement is one of the most expensive items in the annual maintenance budget [73]. Refractory service life is related to gasifier operating temperature, slag properties and coal throughput rate. Despite the improvement in refractory material, the liner life time at Eastman has decreased due to Eastman's increased coal throughput. In 2001, approximate life time per hot liner was 7,000 to 8,000 hours (292–333 days).

The cost of lost production in the Eastman case study was estimated as follows:

- Average unit outage is a 250 MW power plant
- Cost of replacing the power = \$100/MWh
- Cost of an outage about \$ 25,000/h (ex. repair costs)
- Shutdown period (shutdown to return to full load) = 22 days
- Cost of lost production = \$13.2 M.

In this example, increasing the refractory service time by 30% results in almost \$4M of annual saving (only taking into account lost production).

Downtime of the Texaco gasifier at Wabash River Energy Ltd in 2003 due to refractory breach was almost 1% of the year [74]. This is the third biggest issue causing unplanned outages after ash deposition in boiler¹ and syngas cooler tube leaks (Figure 10).

During 2003 at the Polk Power Station IGCC plant planned outage to replace refractory lining was 30 days [75]. Fortunately, it coincided with other major repairs, in this case rewinding generators. However, this coincidence for two major repairs would not always occur. In that case the cost of lost production could be as high as \$18M.

Within the last five years the funding of studies of refractories corrosion in gasification technologies (including developing of the more slag-resistible materials) by the US Department of Energy increased more than 5 times (Figure 11). This gives an indication of the importance of the problem to US gasifier operators. However, it should be noted that US DOE program on refractory corrosion is mostly concentrated on the refractory materials aspects of the problem, rather than on matching the coal slag compositions to the refractories in order to prolong refractory life.

¹ The 2003 “ash deposition in boiler“ issue was an isolated event, as opposed to the other problems which are expected to happen more regularly.

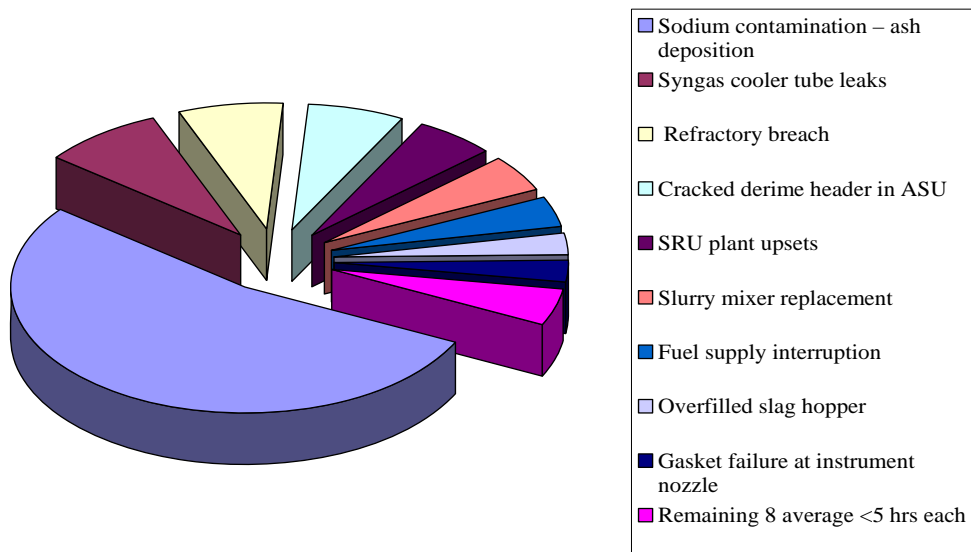


Figure 10. 2003 Gasification Downtime causes at Wabash River Energy LTD [74].

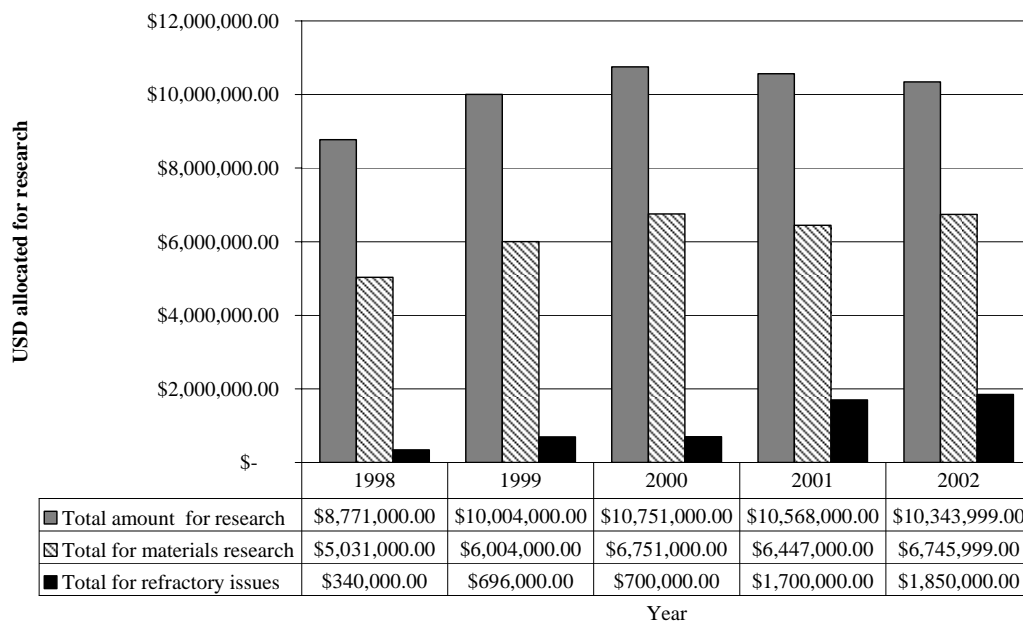


Figure 11: Funding allocated for research by US DOE, Office of Fossil Fuels.

3.2. Mechanism of Slag-Refractory Interactions

The major factors leading to the wear of refractory-based gasifier liners are:

- elevated temperature
- large and/or rapid changes in temperature
- erosion by particulates
- attack of molten slag of variable compositions (as a consequences of variations in feedstock)
- attack by hot corrosive gases, including alkali vapour.

Refractory materials that can withstand these conditions for long periods of time are essential for a continuous, efficient, and reliable gasification process. Two major types of refractories are traditionally used in coal gasifiers: silicon carbide [76-82] and alumina based refractories [71, 82-104] (sintered and/or fused cast alumina-silicate, high alumina, chromia-alumina, chrome-magnesia spinels, alumina-chromia-zirconia).

A number of studies have been conducted to establish the mechanism of refractory degradation from interactions with the coal slag and to predict refractory lifetime. These are summarised in Table 4.

Refractory	Failure mechanism	Author	Institution
Silica Carbide	Chemical dissolution	Easler et al.[78-81, 105, 106]	Argonne National Laboratories
Alumina	Chemical dissolution, Creep cracking	Baker [83, 84]	Argonne National Laboratories
Chromia Alumina	Chemical dissolution	Rawers et al. [107]	Albany Research Centre
Chromia Alumina	Chemical Dissolution	Muan [108, 109]	Pennsylvania State University
Alumina-Magnesia	Slag Erosion	Chon et al. [87]	Hongik University, Seoul
Chromia Alumina	Dissolution of refractory grain boundaries	Rawers et al.[104, 107, 110]	Albany Research Centre
Chromia Alumina	Thermal stress	Rawers et al. [104, 107, 110]	Albany Research Centre

Table 4: Major studies on the mechanism of slag/refractory interactions

The complex nature of slag wear, combining both chemical and physical processes (schematically presented on Figure 12) means that a pure phase equilibria approach (i.e. solely chemical dissolution of ceramic grains and bonding material) is not sufficient to understand the refractory interactions and reactions with coal slags.

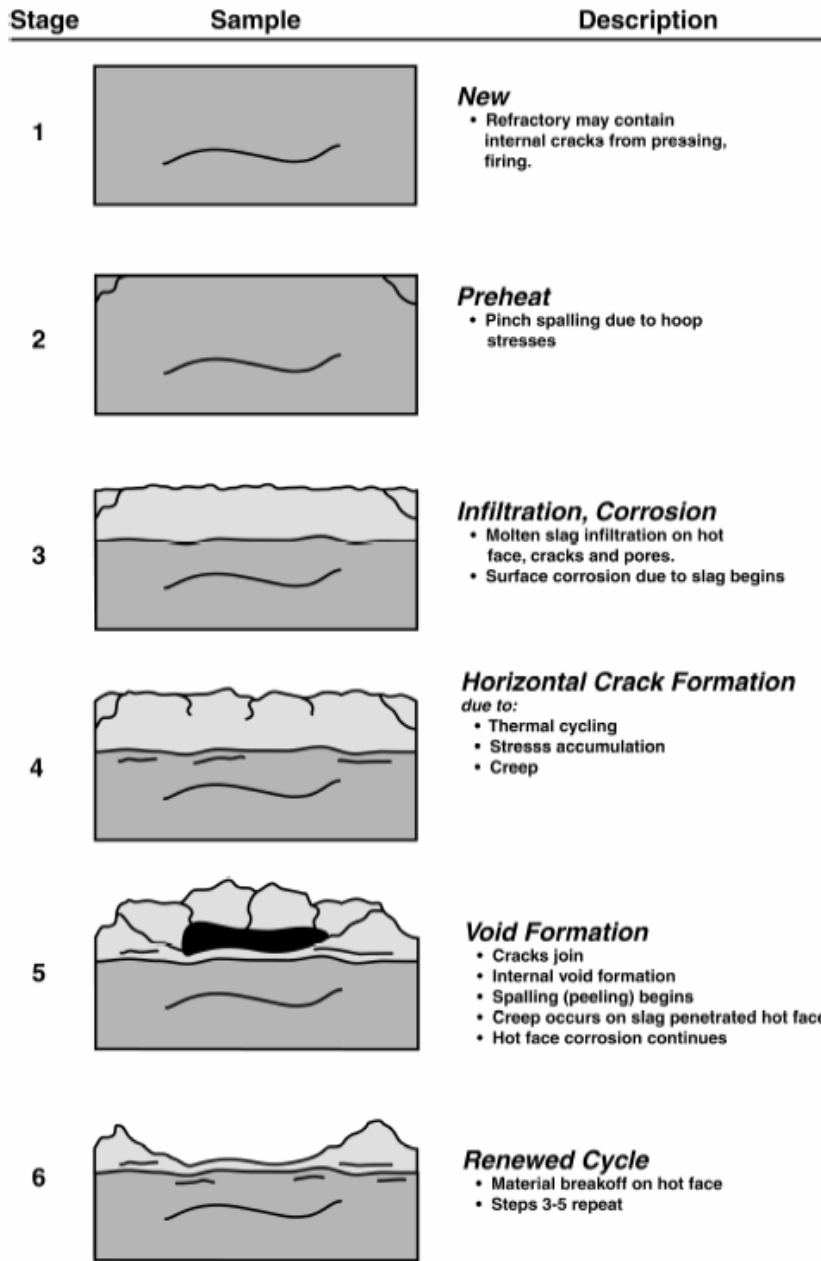


Figure 12: Schematic diagram of refractory degradation mechanism [111]

3.2.1. Chemical Dissolution

For silicon carbide based refractories, chemical dissolution is the major factor responsible for ceramic failure [78-81]. Silicon carbide interacts with iron oxides in

the slag, yielding volatile gases (e.g. CO, SiO) and metallic iron. Therefore, slags with higher iron content will cause higher degradation of SiC-based refractory compared to the slags with low iron content.

The degradation of alumina based refractories in slagging gasifiers occurs by dissolution into molten coal slag [83, 84]. Creep cracking at the hot face is another effect of slag penetration, caused by thermal gradients through the refractory lining.

Rawers et al [107] showed that coal slag can dissolve high chromia alumina sesquioxide refractory from the initial stages of the slag resistance test. A consequence of this dissolution is an alteration in the composition of the slag, and thus its flow behaviour. This change has a potential to disrupt the normal operation of the gasifier [112].

Muan [108, 109] carefully examined high temperature phase equilibria data of relevant ceramic systems (both slag and refractories) at different oxygen partial pressures. It was found that under reducing conditions, there is an increased fraction of divalent chromium in silicate melts (up to several wt %). The increase of Cr²⁺ decreases liquidus and solidus temperatures and consequently decreases refractory resistance to chemical dissolution.

Chemical dissolution is not the only factor affecting the refractory resistance. As shown by Cho and Hong [87], an increase of magnesia in the refractory does increase the chemical resistance to slag corrosion, but decreases the resistance to slag penetration into the ceramic. This decreased resistance makes the refractory more susceptible to slag erosion. Slag penetration into the refractory is an important degradation factor, evident from examination of failed refractory bricks [84, 85, 112]. Such penetration dissolves grain boundaries and decreases the strength of the material.

3.2.2. Thermal Stress

The other important factor in refractory failure is thermal stress of ceramic lining [84, 85, 112]. During thermal expansion of the hot side of refractory lining, high compressive hoop stresses are initiated. These stresses cause micro-cracking of the ceramic. Micro-cracks in the refractory have two important effects. Firstly, they act as stress concentrators, causing growth of bigger cracks and erosion of refractory. Secondly, these micro-cracks promote further slag penetration. Slag penetrated into the refractory due to a difference in thermal expansion coefficients increases the stresses inside the refractory wall and encourages further mechanical degradation of the refractory.

3.3. Tests for Slag–Refractory Interactions

A good understanding of slag–refractory interactions requires proper laboratory procedures. Currently there are two major types of testing procedures for measuring the nature and rate of slag-refractory interactions: static (cup) and dynamic (rotation cylinder or drip) testing.

3.3.1. *Static Testing*

Cup (or static) testing is quite common for the initial estimation of refractory resistivity to slag degradation. During this test, molten slag is placed into a refractory cup and held for a certain time. The cup is then sectioned and examined both visually and with instrumental analytical techniques, such as scanning electron microscopy, electron probe microanalysis and X-Ray diffraction. This type of test has been used at the Albany Research Centre [70, 71, 88, 89, 104, 107, 110] for a large number of their experiments and at University of North Dakota [82] for the initial screening of refractories.

Whilst this technique is efficient in determining inappropriate slag–refractory combinations, a successful cup test does not guarantee that refractory is suitable for the tested slag application. This test uncertainty is a result of the following:

- Cup tests only reflect the chemical corrosion of the slag, no mechanical erosion is taken into account
- During a cup test dissolved refractory material changes the slag composition. Slag reactivity may therefore be affected, leading to slowing down the reaction. In reality, constant slag flow in gasifier does not allow that degree of slag enrichment with refractory material.

3.3.2. *Rotation Bob Test*

The use of the rotation bob test [34, 91, 92, 94, 113] allows simulation of flowing conditions. It therefore allows not only testing of the chemical resistance of the refractory, but also the dependence of refractory wear on slag flow rate. In some cases, where the metallurgical slags were studied [34], there was a critical flow speed, at which the ceramic wear rate was dramatically increased. This was particularly the case for blast furnace slags, which contain both slag and liquid metal phases. Thus, if there is a slag–metal interface contacting the ceramic lining, at some slag flow rates the erosion of the refractories could be several times higher than slag–refractory or metal–refractory interfaces alone.

Whilst the rotating bob test provides a reasonable simulation of practical gasifier conditions, a serious limitation of this test is a potential enrichment of tested slag

sample with refractory residues. This change of slag compositions during an experiment can result in large discrepancies in test results, and consequently have significant impacts on operation of the gasifier.

3.3.3. Flowing Slag Test

To overcome contamination of the testing slag with refractory residues, Hurley and Kleven [82] developed a bench scale test for flowing slag. In this test, studied slag is flowing on an incline made from the refractory to be tested. The constant flow of the fresh slag eliminates the enrichment of the slag with refractory residues in the testing zone. This test showed more realistic results, however the reported design of the experiments shows some limitations of the test. In these experiments, tests can be performed only in an air (oxidising) atmosphere and at only one flow speed for each temperature (as the flow speed is determined by the slag viscosity). Changes in the design to overcome these limitations is possible; however this type of apparatus will require a very expensive set-up.

3.3.4. Other Tests

All of these tests are based on ‘post mortem’ examination of refractory after slag testing. An in-situ test capable for testing the kinetics of slag wetting and dissolution of refractory also has been reported [114, 115]. During this test the weighed refractory rod is slowly immersing into the slag. The changes in the weight of refractory material contacting with molten slag are monitored, particularly at the very first moments of contact. This technique could be useful in research of initial stages of slag–refractory interactions.

3.4. Minimising Slag–Refractory Interactions

There are two ways of minimising the effects of slag–refractory interactions. One is to change the material used to make the refractory, the other is to choose slag compositions compatible with a given refractory lining.

3.4.1. Effects of Refractory Compositions on Refractory Wear

To address the refractory reliability issue, a research team from the Albany Research Centre [89] suggested that slag penetration into refractory could be decreased by

- Changing the wettability of refractory with slag by changing the slag composition or the surface properties of refractory
- Decreasing the level of interconnected porosity in refractory
- Changing the refractory and slag composition to cause a reaction which effectively seals off the refractory surface.

They chose to modify the refractory compositions with small additions of aluminium or chromium phosphates to react with slag and seal off the surface. This approach was quite successful, decreasing the slag penetration by an order of magnitude. However, only limited slag compositions were tested to establish the slag compositional requirements. Therefore, the range of slag composition where these refractory modifications are effective remains unclear.

3.4.2. Effects of Slag Properties on Refractory Wear

There are very few reports in the literature on the effects of chemical composition of slag on refractory resistance. Hannel [76] reported that the decrease in viscosity of slag increases the corrosion of refractory. Such a correlation between slag viscosity and refractory corrosion could be expected because at lower viscosities slag has a higher ability to penetrate microcracks.

An increase of CaO content in slags decreases corrosion resistance of chromia/zirconia refractory [113]. Tests for high-rank and low-rank coal slags by Hurley and Kleven showed that even small quantities of fluxing (e.g. addition of 3wt% Al₂O₃) can significantly (by a factor of three) decrease the corrosivity of the slag. This worked by affecting the viscosity of the slag and the ability of the slag to dissolve the refractory. Although fluxing with alumina may be economically ineffective, coal blending to achieve desired slag composition could possibly be used to achieve this aim.

There is a need for correct refractory matching to slag compositions and operation conditions. If this match could be achieved, refractory lifetimes can be extended, as in the previously described example with alumina fluxing [113]. However, to develop an effective strategy encompassing refractory materials selection, slag composition optimisation and choice of operating conditions, an extensive database of experimental studies and predictive models of slag–refractory interactions are required. No comprehensive and systematic testing of the dependence of slag–refractory interactions on coal slag composition has been reported in the literature. Furthermore, there are no reports of predictive modelling of refractory life as a function of refractory and slag composition and slag flow rate.

3.5. Slag–Refractory Interactions: Summary and Recommendations

Slag–refractory interactions is emerging as one of the important mineral matter topics associated with coal use in slagging gasification technologies. The major mechanisms for slag attack on refractories are understood in general. There is no universal refractory solution for every slag composition. The vast majority of the research reported in the literature is dedicated to the refractory aspect of the problem; the slag

composition aspect has not been investigated. Furthermore, no attempts at modelling slag–refractory interactions have been reported in the literature so far.

To improve the understanding of slag–refractory interactions, systematic data in the following areas are required:

- Studying the slag refractory interactions for a limited number of refractories (eg. chromia–zirconia, alumina–chromia and alumina–chromia–magnesia with and without phosphate additions) using a variety of slags of the most prospective Australian coals. These studies should concentrate on:
 - Effect of slag chemical composition (major elements Si, Al, Ca, Fe) on slag refractory interactions
 - Effect of slag viscosity and flow rate on refractory degradation.
 - Effects of content of minor elements (Na, K, Mg) in slag on refractory degradation.
- Modelling the slag–refractory interactions with a view to incorporate them into gasifier and IGCC process models and (if applicable) to some thermodynamic databases.

As a testing method, it is recommended to use rotating-type tests, paying specific attention to the following details:

- Slag flow speeds should be similar to the slag flow rates in the gasification process
- Saturation of slag with refractory material should be measured and accounted for
- ‘Post mortem’ examination of refractory should include scanning electron microscopy, electron probe microanalysis and X-Ray diffraction examinations to determine the detailed mechanisms and of slag–refractory interactions for specific refractory and slag compositions.

Achievement of the most economical operation of gasifiers, from both slag flow and refractory wear point of view, requires a strategy for optimising the coal composition (by blending or fluxing). This strategy could be developed on the basis of a refractory degradation model and systematic information regarding slag composition effects on slag–refractory interactions. This work would be complementary to, and synergistic with, the extensive work already conducted on composition effects on slag viscosity and, in practice, a solution to both issues (slag viscosity and slag–refractory interactions) is required.

4. ENVIRONMENTAL ISSUES

4.1. Leachability

The coal throughput for an average gasifier is of the order of 2,000 tonnes per day. This will produce approximately 200 tonnes of slag per day. For 250 operational days it results in 50,000 tonnes of slag per year. At these scales even small concentrations of heavy metals in coal slag results in high quantities (e.g for an average manganese concentration of 0.05% in coal ash, the total annual amount of manganese contained in the coal slag could be almost 25 tonnes per year). Therefore, slag stability in terms of leachability of heavy metals is an absolutely essential condition for safe disposal or beneficial reuse. For this reason a number of studies have been reported on the leachability of heavy metals and other toxic elements from the coal gasification slag

Whetherold et al. [116] studied the leachability of slags from a Texaco gasifier using Illinois No6 coal as a feedstock. The results showed that the heavy metals are stable inside the slag. Similar studies of the leachability of slag from a BGL gasifier [117] concluded that the slag is a highly inert material presenting no hazard to the environment. Research on the solid by-product of a Shell gasifier [118] confirmed that the slag and flyslag are environmentally clean, and suitable for several possible applications of these materials, including use in concrete, asphalt, lightweight aggregate and cement production. The end-use products readily meet environmental requirements.

Comparison of gasification slag and combustion ash [119] showed that the concentrations of most trace elements in leachate from slag and pf bottom ash were below current or proposed drinking water levels. In contrast, the concentrations of As, Cd, Cr, Se, Zn, Mn, Cu, and SO_4^{2-} in leachate from combustion fly ashes exceeded drinking water levels.

Most of the refractories used in gasifiers are based on chromia (Cr_xO_y). As discussed earlier, refractory wear mechanisms involve both mechanical erosion and chemical dissolution of ceramic. Therefore, the discharged coal slag is likely to be heavily enriched with both chromia particles and chromia dissolved in the slag. The latter is unlikely to have an environmental impact (due to high stability of slag); however, chromia particles not dissolved by slag could be a potential danger if they are released from the slag. The reported work on the toxicity of chromium waste sites [120-122] showed that air could oxidise trivalent chromia (which is a biologically inert material and the most likely form of chromium in slag) into highly toxic hexavalent chromium. Presence of CaO (a fluxing agent in many gasification operations) increases this rate of oxidation [121]—whether this is enough to be a

significant problem is unclear. The possible oxidation of chromia inclusions requires better understanding and evaluation of its practical scales and environmental impacts.

4.2. Toxicity

The plant toxicity of ash and slag wastes was reported by Jenner et al. [123]. In those studies, Duckweed (*Lemna minor*) was used for testing single elements and leachates of coal ashes and slags by expressing growth as surface coverage. The EC₅₀ (the molar concentration of an element producing 50% of the maximum possible response for that element) for Cd, Cu, Zn, As(III), As(V), Se(IV), Se(VI), SeO₂ were 0.86, 2.2, 4.4, 8.4, 297, 21, 67, 37 mmol/L, respectively. Therefore the sensitivity of the test plant was sufficient to determine the toxic effects of leachates. Leachates of pulverised coal fuel ash, including ashes from low NO_x pf boilers and of coal gasification slag (CGS) were tested. The concentrations of elements in leachates of the pulverised coal fuel (pf) ash from a low NO_x pf system were higher than those in leachates of conventional pf ash. The leaching of anions from pf ash was more rapid than the leaching of cations. Coal gasification slags showed minimal element leaching and tests did not indicate any plant toxicity associated with these slags.

To investigate the potential adverse health effects of slag dust, studies on the oral toxicity of slags were conducted on rats [124]. During this research, slag from a coal gasification plant was added to a rat diet (5% slag). Exposure to this slag had no effect on the absorption, retention, and organ distribution of Cd, Hg, or Mn. In acute toxicity studies, this exposure had no effect on LD₅₀ (the lethal dose of a compound for 50% of animals exposed) values obtained 8 days after oral administration of Cd, Hg, or Mn to rats of different ages. Oral exposure to slag in the diet had almost no effect on the toxicokinetics (the absorption, distribution, metabolism, storage, and excretion of chemicals) and toxicity of Cd, Hg, and Mn. This was explained by the low level or low bioavailability of elements from the slag.

All of these studies indicated that slag from coal gasification is a non-hazardous material, capable of stable immobilisation of potentially toxic elements contained in coal.

4.3. Recommendations on Studies of Environmental Impact by Slag

Coal gasification slag is a very stable material, however, at this stage further detailed studies of the leachability of heavy metals from the slag produced from coal gasifiers are under consideration by corresponding CCSD program.

However, some preliminary studies on chromia inclusions in gasification coal slag should be done in conjunction with the slag–refractory interactions investigations.

These studies will allow evaluation of the importance of this problem and make a decision on the necessity of further studies.

5. RECOMMENDATIONS

Slag flow behaviour is the most important mineral matter aspect of coal use in entrained-flow gasification. The key issues associated with slag flow behaviour have been well addressed in the CCSD program for the gasification of Australian coals. The remaining areas in this field (in the order of importance) are:

- Validation of existing slag flow models with existing experimental data
- Developing a Tcv prediction tool based on slag phase composition
- Integration of these slag flow models into coal evaluation industry tools
- Developing a slag flow behaviour model explaining the phenomenon, rather than simply describing it by a large number of empirical coefficients to apply over whole range of Australian and overseas coals,
- Developing a model of slag flow inside the gasifier walls, including thickness of slag layer and slag discharge rates.

By validating the existing slag flow models, developing Tcv prediction tools and incorporating these into industry models, it would be possible to develop a complete strategy for assessing coals, optimising fluxing and blending strategies.

The other important issue is slag–refractory interactions. To understand truly the issues and to achieve a breakthrough in this area, systematic studies of the effects of chemical compositions on the rate of refractory degradation are required. The experimental work in this area must be combined with modelling of slag–refractory interactions. This program should aim to match the gasifier refractory and the coal slag composition to substantially increase gasifier reliability and minimise operation expenses, such as refractory service.

As a first step, it is recommended to develop a research program for the slag–refractory interactions, concentrating on the effects of composition on slag corrosivity and in the matching of coal slag compositions to appropriate refractory materials.

6. REFERENCES

1. A G Collot. *Matching gasifiers to coals*, CCC/65 (2002).
2. H J Hurst, L Elliott and J H Patterson. *Evaluation of the slagging characteristics of Australian bituminous coals for use in slagging gasifiers*, 15th Annual International Pittsburgh Coal Conference (1998). pp.421-439.
3. J H Patterson and H J Hurst. *Ash and slag qualities of Australian bituminous coals for use in slagging gasifiers*, Fuel **79(13)**, 1671-1678 (2000).
4. J H Patterson, H J Hurst and F Novak. *Suitability of Australian bituminous coals for use in slagging gasifiers*, 13th Annual International Pittsburgh Coal Conference (1996). pp.1449-1454.
5. J H Patterson, H J Hurst and A Quintanar. *Slag compositional limits for coal use in slagging gasifiers*, 19th Annual International Pittsburgh Coal Conference (2002). pp.1818-1836.
6. J H Patterson, H Hurst, F Novak, L Elliott and H Tran. *Evaluation of Australian bituminous coals for advanced power generation: Slagging characteristics for Integrated Gasification-Combined Cycle (IGCC)*, ACARP Project C4058 (1998).
7. S Vargas, F J Frandsen and K Dam-Johansen. *Rheological properties of high-temperature melts of coal ashes and other silicates*, Progress in Energy and Combustion Science **27(3)**, 237-429 (2001).
8. K C Mills. *Viscosities of molten slags*, National Physics Laboratory, (1992).
9. G Urbain and M Boiret. *Viscosities of Liquid Silicates*, Ironmaking & Steelmaking **17(4)**, 255-260 (1990).
10. G Urbain, Y Bottinga and P Richet. *Viscosity of liquid silica, silicates and alumino-silicates*, Geochimica Et Cosmochimica Acta **46(6)**, 1061-1072 (1982).
11. R C Streeter, E K Diehl and H H Schobert. *Measurement and Prediction of Low-Rank Coal Slag Viscosity*, Preprints of Papers - American Chemical Society, Division of Fuel Chemistry **28(4)**, 174-195 (1983).
12. H H Schobert, E K Diehl and R C Streeter. *Current Studies in Coal Ash Slag Viscosity*, United States Department of Energy, Morgantown Energy Technology Center (Report) DOE/METC (1982).
13. G Urbain. *Viscosite de Liquides Silice-Alumine-Oxydes Na et K Mesures et Estimations*, Revue Internationale Des Hautes Temperatures Et Des Refractaires **22(1)**, 39-45 (1985).
14. D H H Quon, S S B Wang and T T Chen. *Viscosity Measurements of Slags from Western Canadian Coals*, Journal of Engineering for Gas Turbines and Power, Transactions of the ASME **107(3)**, 803-806 (1985).
15. D H H Quon, S S B Wang and T T Chen. *Viscosity Measurements of Slags from Pulverized Western Canadian Coals in a Pilot-Scale Research Boiler*, Fuel **63(7)**, 939-942 (1984).
16. J Chen, S Greenberg and R B Poeppel. *Viscosity of coal slags as a function of composition, temperature, and oxygen partial pressure*, Argonne National Laboratory Report number ANL/FE-83-80 (1984).

17. J M Rhines, K C Mill and F H Putland. *The physical properties of slags formed during coal gasification*, High Temperatures - High Pressures **17(2)**, 173-83 (1985).
18. K C Mills and J M Rhine. *The Measurement and Estimation of the Physical-Properties of Slags Formed During Coal-Gasification .2. Properties Relevant to Heat-Transfer*, Fuel **68(7)**, 904-910 (1989).
19. H J Hurst, J H Patterson and A Quintanar. *Viscosity measurements and empirical predictions for some model coal gasifier slags-II*, Fuel **79(14)**, 1797-1799 (2000).
20. H J Hurst, F Novak and J H Patterson. *Viscosity measurements and empirical predictions for some model gasifier slags*, Fuel **78(4)**, 439-444 (1999).
21. H J Hurst, F Novak and J H Patterson. *Viscosity measurements and empirical predictions for fluxed Australian bituminous coal ashes*, Fuel **78(15)**, 1831-1840 (1999).
22. H J Hurst, F Novak and J H Patterson. *Phase diagram approach to the fluxing effect of additions of CaCO₃ on Australian coal ashes*, Energy and Fuels **10(6)**, 1215-1219 (1996).
23. J H Patterson, H J Hurst, A Quintanar, R K Boyd and H Tran. *The slag flow characteristics of Australian bituminous coals in entrained-flow slagging gasifiers*, Proceedings - Annual International Pittsburgh Coal Conference **18th**, 1686-1708 (2001).
24. J H Patterson, H J Hurst and A Quintanar. *Slag compositional limits for coal use in slagging gasifiers*, Final Report for ACARP Project C10062 (2002).
25. J P Hurley, T M Strobel and J W Nowok. *The effects of atmosphere and additives on coal slag viscosity*, 211th ACS National Meeting, March 24-28, New Orleans, LA, (1996). p.126.
26. J P Hurley, T M Watne and J W Nowok. *The effects of atmosphere and additives on coal slag viscosity*, Preprints of Papers - American Chemical Society, Division of Fuel Chemistry **41(2)**, 691-4 (1996).
27. J W Nowok. *Viscosity and Structural State of Iron in Coal Ash Slags under Gasification Conditions*, Energy and Fuels **9(3)**, 534-9 (1995).
28. K S Vorres, S Greenberg and R B Poeppel. *The viscosity of synthetic coal slags as a function of composition, temperature and oxygen partial pressure*, 2nd International Symposium on Metallurgical Slags and Fluxes (1984). pp.949-57.
29. N N Kinaev and J H Patterson. *Viscous Behaviour of Australian Coal Ash Slags with High Iron and Low Silica/Alumina Ratio*, 21st Annual International Pittsburgh Coal Conference, Osaka, Japan (2004). <http://www.ccsd.biz/publications/journals.cfm?PubID=543>
30. G J Browning, G W Bryant, H J Hurst, J A Lucas and T F Wall. *An Empirical Method for the Prediction of Coal Ash Slag Viscosity*, Energy and Fuels **17(3)**, 731-737 (2003).
31. H J Hurst, F Novak and J H Patterson. *Viscosity models for fluxed Australian bituminous coal ashes*, 5th International Conference on Molten Slags, Fluxes and Salts '97, Sydney, Jan. 5-8 (1997). pp.873-876.
32. A Kondratiev and E Jak. *Predicting coal ash slag flow characteristics (viscosity model for the Al₂O₃-CaO-'FeO'-SiO₂ system)*, Fuel **80(14)**, 1989-2000 (2001).

33. A Kondratiev and E Jak. *Applications of the coal ash slag viscosity model for the slagging gasification technologies (viscosity model in the Al₂O₃-CaO-FeO-SiO₂ system)*, 18th Annual International Pittsburgh Coal Conference (2001). pp.1709-1723.
34. S Sun, L Zhang and S Jahanshahi. *From viscosity and surface tension to Marangoni flow in melts*, Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science **34B(5)**, 517-523 (2003).
35. I Vladimirov, S Christie and E Jak. *Computer modelling of physical-chemical properties of complex coal ash slag systems in multi-dimensional compositional space*, 18th Annual International Pittsburgh Coal Conference (2001). pp.2340-2353.
36. J H Patterson and T Do. *Survey of the Suitability of Export Thermal Coals for IGCC Use*, Final Report for ACARP Project C12056 (2004).
37. J H Patterson, H J Hurst and A Quintanar. *Slag compositional limits for coal use in slagging gasifiers*, Proceedings - Annual International Pittsburgh Coal Conference **19th**, 1818-1836 (2002).
38. M S Oh, D D Brooker, E F de Paz, J J Brady and T R Decker. *Effect of crystalline phase formation on coal slag viscosity*, Fuel Processing Technology **44(1-3)**, 191-9 (1995).
39. M S Oh, E F de Paz, D D Brooker, J J Brady and T R Decker. *Effect of crystalline phase formation on coal slag viscosity*, Preprints of Papers - American Chemical Society, Division of Fuel Chemistry **38(4)**, 1263-9 (1993).
40. G J Browning, D G Roberts, J A Lucas, T F Wall, M Ashizawa and Y Oki. *The heterogeneity of slags and slag flow in coal-fired entrained-flow gasifiers*, 18th Annual International Pittsburgh Coal Conference (2001). pp.1974-1984.
41. A Kondratiev and E Jak. *Modeling of viscosities of the partly crystallized slags in the Al₂O₃-CaO-FeO-SiO₂ system*, Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science **32B(6)**, 1027-1032 (2001).
42. Kondratiev A, Jak E, "A quasi-chemical viscosity model for fully liquid slags in the Al₂O₃-CaO-FeO-SiO₂ system", Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science, **36B(5)**,: 623-638 (2005).
43. I Avramov, C Russel and R Keding. *Effect of chemical composition on viscosity of oxide glasses*, Journal of Non-Crystalline Solids **324(1-2)**, 29-35 (2003).
44. I Avramov, E D Zanotto and M O Prado. *Glass-forming ability versus stability of silicate glasses. II. Theoretical demonstration*, Journal of Non-Crystalline Solids **320(1-3)**, 9-20 (2003).
45. I Avramov and I Gutzow. *Relaxation kinetics of glasses and glass-forming melts*, Journal of Non-Crystalline Solids **298(1)**, 67-75 (2002).
46. I Avramov and G Voelksch. *Near-surface crystallization of cordierite glass*, Journal of Non-Crystalline Solids **304(1-3)**, 25-30 (2002).
47. I Avramov, E D Zanotto and M O Prado. *Glass forming ability (on cooling) and stability (on heating)*, Glass Science and Technology **75**, 60-65 (2002).
48. I Avramov. *Pressure dependence of viscosity of glassforming melts*, Journal of Non-Crystalline Solids **262(1-3)**, 258-263 (2000).

49. I Avramov. *Viscosity of glass-forming melts*, Journal of Non-Crystalline Solids **238(1-2)**, 6-10 (1998).
50. I Avramov. *Viscosity of Undercooled Melts*, Journal of Materials Science Letters **13(18)**, 1367-1369 (1994).
51. I Avramov. *Influence of Disorder on Viscosity of Undercooled Melts*, Journal of Chemical Physics **95(6)**, 4439-4443 (1991).
52. I Avramov. *Pressure-Dependence of Shear Viscosity*, Physica Status Solidi a-Applied Research **120(1)**, 133-138 (1990).
53. I Avramov and A Milchev. *Effect of Disorder on Diffusion and Viscosity in Condensed Systems*, Journal of Non-Crystalline Solids **104(2-3)**, 253-260 (1988).
54. I Avramov, I Gutzow and E Grantscharova. *Crystallization Kinetics and Rheology of Undercooled Melts*, Journal of Crystal Growth **87(2-3)**, 305-310 (1988).
55. J Watt and F Fereday. *Flow Properties of Slags Formed from Ashes of British Coals-1*, Journal of Institute of Fuel **42(338)**, 99-103 (1969).
56. G Urbain, F Cambier, M Deletter and M R Anseau. *Viscosity of Silicate Melts*, Transactions and Journal of the British Ceramic Society **80(4)**, 139-141 (1981).
57. G Urbain. *Viscosity Estimation of Slags*, Steel Research **58(3)**, 111-116 (1987).
58. D P Kalmanovitch, A Sanyal and J Williamson. *Slagging in Boiler-Furnaces - a Prediction Technique Based on High-Temperature Phase-Equilibria*, Journal of the Institute of Energy **59(438)**, 20-23 (1986).
59. P V Riboud, Y Roux, L-D Lucas and H Gaye. *Fachber Huettenprax Metalweiterverarb* **19(10)**, 859-69 (1981).
60. L Zhang, S Jahanshahi, S Sun, C Chen, B Borke, S Wright and A Somerville. *CSIRO's multiphase reaction models and their industrial applications*, Jom-Journal of the Minerals Metals & Materials Society **54(11)**, 51-56 (2002).
61. L Zhang and S Jahanshahi. *Modelling viscosity of alumina-containing silicate melts*, Scandinavian Journal of Metallurgy **30(6)**, 364-369 (2001).
62. S Wright, L Zhang, S Y Sun and S Jahanshahi. *Viscosities of calcium ferrite slags and calcium alumino-silicate slags containing spinel particles*, Journal of Non-Crystalline Solids **282(1)**, 15-23 (2001).
63. L Zhang, S Y Sun and S Jahanshahi. *Molecular dynamics simulations of silicate slags and slag-solid interfaces*, Journal of Non-Crystalline Solids **282(1)**, 24-29 (2001).
64. L Zhang and S Jahanshahi. *Review and modeling of viscosity of silicate melts: Part I. Viscosity of binary and ternary silicates containing CaO, MgO, and MnO*, Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **29(1)**, 177-186 (1998).
65. L Zhang and S Jahanshahi. *Review and modeling of viscosity of silicate melts: Part II. Viscosity of melts containing iron oxide in the CaO-MgO-MnO-FeO-Fe₂O₃-SiO₂ system*, Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **29(1)**, 187-195 (1998).
66. L Zhang, S Jahanshahi, H J Hurst and J H Patterson. *A predictive model for viscosity of molten coal ash slags*, 18th Annual International Pittsburgh Coal Conference (2001). pp.2321-2330.

67. H J Hurst, F Novak and J H Patterson. *Prediction of the Amount of Calcium Carbonate needed for the successful slag tapping of some Australian Coals in a Slagging Gasifier*, 6th Australian Coal Science Conference, Newcastle, Australia (1994). pp.222-229.
68. K C Mills and J M Rhine. *The Measurement and Estimation of the Physical-Properties of Slags Formed During Coal-Gasification .1. Properties Relevant to Fluid-Flow*, Fuel **68(2)**, 193-200 (1989).
69. S Wright, L Zhang, S Sun and S Jahanshahi. *Viscosity of a CaO-MgO-Al₂O₃-SiO₂ melt containing spinel particles at 1646 K*, Metallurgical and Materials Transactions B-Process Metallurgy and Materials Processing Science **31(1)**, 97-104 (2000).
70. C P Dogan, J P Bennett, K-S Kwong and R E Chinn. *Refractory loss in slagging gasifiers*, Proceedings of [the] Unified International Technical Conference on Refractories, Biennial Worldwide Congress, 7th, Cancun, Mexico, Nov. 4-7, 2001 **1**, 270-275 (2001).
71. K S Kwong, C P Dogan, J P Bennett, R E Chinn, C L Dahlin, E A Krabbe and A V Petty. *Functional design of refractories for slagging gasifiers*, 19th Annual International Pittsburgh Coal Conference (2002). pp.1514-1522.
72. N Moock. *Eastman Gasification Services Company Reliability Modeling*, Gasification Technologies Conference, San Francisco (2003).
73. S Hrivnak. *Eastman Chemical Company: Fine Tuning to Improve Availability and Reliability of Coal Based Gasification*, Gasification Technologies 2001, San Francisco (2001).
74. C G Keeler. *Operating Experience at the Wabash River Repowering Project*, Gasification Technologies Council Technology Conference, San-Francisco (2003).
75. J D McDaniel and M Hornick. *Gasification Technologies Council Technology Conference*, Gasification Technologies Council Technology Conference, San Francisco (2003).
76. S E Hannel, K Breder and D L Joslin. *Effects of coal slag corrosion on the mechanical properties of sintered α -silicon carbide*, Ceramic Engineering and Science Proceedings **18(3)**, 513-523 (1997).
77. M L Auger, A Sengupta and V K Sarin. *Coal slag protection of silicon carbide with chemically vapor deposited mullite coatings*, Journal of the American Ceramic Society **83(10)**, 2429-2435 (2000).
78. T E Easler. *Effects of coal gasification environments on corrosion behavior and mechanical properties of siliconized silicon carbide*, Argonne Natl. Lab., Report ANL/FE-85-6 (1985).
79. T E Easler. *Corrosion behavior and mechanical properties of silicon carbide exposed to a coal gasification environment*, Argonne Natl. Lab., Report ANL/FE-84-21 (1985).
80. T E Easler. *Comparison of results of 200- and 500-h exposures of silicon carbide to a slagging coal gasification environment*, Argonne Natl. Lab., Report ANL/FE-85-13 (1986).
81. T E Easler and J M Hobday. *Mechanical properties and corrosion behavior of structural ceramics exposed to coal gasification environments*. In: Materials Science Monographs, Volume 38C. (1987). pp.2387-96.

82. J P Hurley and P L Kleven. *Bench-scale measurements of refractory corrosion by flowing corrodents*, Proceedings of [the] Unified International Technical Conference on Refractories, Biennial Worldwide Congress, 7th, Cancun, Mexico, Nov. 4-7, 2001 **3**, 1667-1681 (2001).
83. W T Bakker. *Wear of refractories in slagging gasifiers*, Proc. - Corros.-Erosion-Wear Mater. Emerging Fossil Energy Syst., 377-400 (1982).
84. W T Bakker. *Refractories for coal gasification*. In: Materials Science Monographs, Volume 38C. (1987). pp.2355-70.
85. W T Bakker, S Greenberg, M Trondt and U Gerhardus. *Refractory practice in slagging gasifiers*, American Ceramic Society Bulletin **63(7)**, 870-6 (1984).
86. U Chon, H G Kim, S K Jeong, E H Lee, J-C Bae, T I Kang, H K Lee and S Kim. *Refractory damage in tapping hole of Corex melter-gasifier*, 7th Unified International Technical Conference on Refractories, Biennial Worldwide Congress, Cancun, Mexico, Nov. 4-7 (2001). Volume 3, pp.1496-1516.
87. M-K Cho and G-G Hong. *Effects of MgO content of spinel on the reaction of spinel with CaO-Al₂O₃-SiO₂ slag*, Yoo Hakhoechi **36(4)**, 410-416 (1999).
88. C P Dogan, J P Bennett, K-S Kwong, R E Chinn and C L Dahlin. *Improved refractories for slagging gasifier applications*, Advances in Science and Technology (Faenza, Italy) (2003). Volume 35, pp.217-224.
89. C P Dogan, K-S Kwong, J P Bennett and R E Chinn. *Improving refractory service life in slagging coal gasifiers*, 18th Annual International Pittsburgh Coal Conference (2001). pp.677-686.
90. C P Dogan, K-S Kwong, J P Bennett, R E Chinn and C L Dahlin. *Improved refractory materials for slagging coal gasifiers*, 27th International Technical Conference on Coal Utilization & Fuel Systems (2002). pp.1167-1176.
91. S Greenberg and R B Poeppel. *Corrosion of ceramic refractories exposed to synthetic coal slags by means of the rotating-cylinder technique*, Argonne Natl. Lab., Report ANL/FE-85-15 (1986).
92. S Greenberg and R B Poeppel. *Corrosion of refractories in a synthetic coal slag*, Argonne Natl. Lab., Report EPRI-AP-4589 (1986).
93. Z Guo, F Li and Y Zhu. *Cr₂O₃-Al₂O₃-ZrO₂ system refractories for slagging coal gasifier*, China's Refractories **2(3)**, 34-8 (1993).
94. Z Q Guo. *Corrosion resistance of high-chrome refractories exposed to molten acidic coal-ash*, Interceram **42(4)**, 211-12, 214-16 (1993).
95. J P Hurley, J P Kay, K D Williams and N S Bornstein. *Measurements of the corrosion of two ODS alloys by flowing coal slag*, Proceedings of Electrochemical Society **16**, 255-263 (2003).
96. J P Hurley and J W Nowok. *Conditions for testing the corrosion rates of ceramics in coal gasification systems*, Proceedings of the Tenth Annual Conference on Fossil Energy Materials, (1996). pp.181-191.
97. C R Kennedy. *Selection of refractories for slagging coal-conversion systems*, 4th Annual Conference on Materials for Coal Conversion and Utilization (1979). pp.IV/18-IV/22.
98. C R Kennedy. *Selection of refractories for slagging coal-conversion systems*, 5th Annual Conference on Materials for Coal Conversion and Utilization (1980). pp.IV-13/IV-17.

99. C R Kennedy. *Compatibility of water-cooled refractories with a basic coal-ash slag at 1500 DegC*, Journal of Materials for Energy Systems **2(2)**, 11-20 (1980).
100. C R Kennedy. *Coal slag-refractory compatibility studies: progress to date*, Ceramic Engineering and Science Proceedings **2(11-12)**, 1156-70 (1981).
101. C R Kennedy, R Swaroop, D J Jones, R J Fousek, R B Poeppel and D Stahl. *Evaluation of ceramic refractories for slagging gasifiers: summary of progress to date*, Report (1978).
102. C R Kennedy and R B Poeppel. *Corrosion resistance of refractories exposed to molten acidic coal-ash slags*, Interceram **27(3)**, 221-6 (1978).
103. C R Kennedy, S W Kreis, R B Poeppel and R A Laskiewicz. *Utilization of coal slag from pressurized coal-gasification plants*, Journal of Materials for Energy Systems **2(1)**, 51-4 (1980).
104. J Rawers, K Collins and M Peck. *Oxides reactions with a high-chrome sesquioxide refractory*, Journal of Materials Science **36(20)**, 4837-4843 (2001).
105. T E Easler and R B Poeppel. *Corrosion of ceramics in heat exchanger applications*, Symposium on High Temperature Corrosion in Energy Systems (1985). pp.269-80.
106. T E Easler, C Tan and L M Putz. *Influence of oxidizing and reducing environments on coal slag-induced corrosion of silicon carbide ceramics*, Argonne Natl. Lab., Report ANL/FE-85-11 (1985).
107. J Rawers, L Iverson and K Collins. *Initial stages of coal slag interaction with high chromia sesquioxide refractories*, Journal of Materials Science **37(3)**, 531-538 (2002).
108. A Muan. *Thermodynamic properties and phase relations for refractory-slag reactions in slagging coal gasifiers*, Oak Ridge National Laboratory, Report ORNL/Sub-80-09006/01 (1987).
109. A Muan. *Equilibrium relations with a bearing on refractory corrosion in slagging coal gasifiers*, 2nd Symposium on High Temperature Materials Chemistry (1983). Volume 83-7, pp.339-48.
110. J Rawers, J Kwong and J Bennett. *Characterizing coal-gasifier slag-refractory interactions*, Materials at High Temperatures **16(4)**, 219-222 (1999).
111. Anon. *Improved Refractory Materials for Coal Gasifiers*. U. S. Department of Energy and EPRI, Advanced Research Materials Program, (2002), 4.pp.
112. P J C Bloem. *Lining in coal-gasification reactors*, Kema Scientific & Technical Reports **8(6)**, 375-381 (1990).
113. Z-Q Guo, B-Q Han and H Dong. *Effect of coal slag on the wear rate and microstructure of the ZrO₂-bearing chromia refractories*, Ceramics International **23(6)**, 489-496 (1997).
114. D Xie and T Tran. *Studies of dynamic refractory-slag interactions using in-situ gravimetric technique*, 7th Unified International Technical Conference on Refractories, Biennial Worldwide Congress, Cancun, Mexico, Nov. 4-7, 2001 (2001). Volume 3, pp.1418-1431.
115. D Xie, T Tran and S Jahanshahi. *In-situ gravimetric studies of wetting, penetration and wear of refractories by molten slags*, High Temperature Materials and Processes (London, United Kingdom) **20(3-4)**, 293-301 (2001).

116. R G Wetherold, R M Mann, C E Hudak, R V Collins, T W Hoskings and K W Lee. *Environmental characterization of the Texaco Coal-Gasification Process at Ruhrkohle/Ruhrchemie in Oberhausen-Holten, Federal Republic of Germany*, Report EPRI-AP-2811 (1983).
117. B H Cooke and M R Taylor. *The environmental benefit of coal gasification using the BGL gasifier*, Fuel **72(3)**, 305-14 (1993).
118. R T Perry, J A Salter, D C Baker, M W Potter, C M Thompson and A G Eklund. *Environmental characterization of the Shell coal gasification process. III. Solid by-products*, 7th Annual International Pittsburgh Coal Conference (1990). pp.269-78.
119. R R Turner and P D Lowry. *Comparison of coal gasification and combustion residues*, Journal of Environmental Engineering (Reston, VA, United States) **109(2)**, 305-20 (1983).
120. A H Stern, J A Fagliano, J E Savrin, N C G Freeman and P J Liroy. *The association of chromium in household dust with urinary chromium in residences adjacent to chromate production waste sites*, Environmental Health Perspectives **106(12)**, 833-839 (1998).
121. K Pillay, H von Blottnitz and J Petersen. *Ageing of chromium(III)-bearing slag and its relation to the atmospheric oxidation of solid chromium(III)-oxide in the presence of calcium oxide*, Chemosphere **52(10)**, 1771-1779 (2003).
122. J A Fagliano, J Savrin, I Udasin and M Gochfeld. *Community exposure and medical screening near chromium waste sites in New Jersey*, Regulatory Toxicology and Pharmacology **26(1)**, S13-S22 (1997).
123. H A Jenner and J P M Janssen-Mommen. *Duckweed Lemna minor as a tool for testing toxicity of coal residues and polluted sediments*, Archives of Environmental Contamination and Toxicology **25(1)**, 3-11 (1993).
124. K Kostial, M Blanusa, T Maljkovic, D Kello, I Rabar and J F Stara. *Effect of a metal mixture in diet on the toxicokinetics and toxicity of cadmium, mercury and manganese in rats*, Toxicology and Industrial Health **5(5)**, 685-98 (1989).