

IGCC Solids Disposal and Utilisation

Final Report for ANLEC project 5-0710-0065

A Y Ilyushechkin, D G Roberts, D French, and D J Harris

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Executive Summary

Overview

Gasification technologies offer a pathway to achieve higher efficiencies and lower emissions than current coal-fired power generation technologies. Most current commercial and demonstration-scale integrated gasification combined cycle (IGCC) projects are based on entrained flow gasification of coal, which is designed to melt the mineral matter in the fuel and produce a glassy slag for storage, use or disposal.

There is an expectation that slags produced by coal-fired gasifiers will be environmentally benign. If this is so, there should be no major issues related to the use or disposal of these materials. Recent work, however, has identified some trace species that can leach from gasification-derived slags. Coal and process-specific issues may also affect the nature and extent of such leachability. While there is some international experience with gasification slags, the handling, disposal and use of gasification by-products in Australia is complicated by the uncertainty of legislative and other requirements of gasifier operators.

This project begins the process of identifying and addressing the issues associated with slag disposal and use that are of direct relevance to Australian gasification projects, using Australian coals under Australian technology and market conditions.

The report begins with a review of legislation and regulations relating to disposal or use of gasification by-products. The review includes an assessment of available data, experience, regulations and outcomes pertaining to slag management practices of existing international IGCC projects, international coal gasification-based chemical industry practices, and relevant technologies such as iron and steel making. The information is presented in the context of current practices for management of solid wastes from existing coal combustion-based processes that are more familiar to the Australian power sector.

The second part of the report presents the results of a preliminary experimental program that compares the properties of industrially-produced and laboratory-produced slag samples. These initial results help us begin to understand how to assess the environmental performance of gasification-derived solid wastes, as well as their suitability for use in specific industries.

Review of legislation and current practice

The use or disposal of gasification-derived solids in Australia is not specifically covered by any legislation, permitting program, or guidelines. However, they are likely to be assessed initially in the same manner as coal combustion products, such as fly ash and bottom ash. If this is the case, then gasification-derived solids will be classified as a waste rather than a resource; but, as in the case of coal ash, there do not appear to be any specific legislative barriers to reuse.

Knowledge of the characteristics of slags produced from gasification of Australian coals is limited. This, combined with the relative lack of Australian experience regarding coal gasification, means that such slags are more likely to be classified according to their origin (i.e. as a coal use product) rather than their physical and chemical properties as a glassy, and, in most cases, inert, material.

This review included a survey of several Australian power generators, ash producers and users to assess current practices and issues associated with coal combustion by-product use and disposal.

The survey was conducted by an industry consultant. The outcomes were used to identify where current guidelines, regulations and industry practices may be applicable (or problematic) to gasification slags and by-products.

Key outcomes of the review are summarised below:

Assessment of the relevance of current Australian and international regulations to gasification-derived material

- No current Australian procedures or regulations govern the use and disposal of gasifier slags. These slags could be expected to have similar use properties to metallurgical slags; however, current practice relates use assessments directly to the source industry sector. More specific characterisation procedures may be needed to recognise the relatively benign form of trace elements and low leachability of these materials.
- State regulations vary considerably, which may affect the classification, disposal and use of slags and fly ashes.
- Several leaching tests can be used to determine the environmental performance of fly ash, slag, etc. The tests vary significantly in their stated aims and techniques, and therefore their applicability and relevance. Standardised leaching tests need to be developed that can realistically assess the likely environmental behaviour of gasification residues.

Use options for gasification-derived slags

- As with blast furnace slags, the most immediately prospective application of IGCC slags from Australian coal appears to be in the cement industry and in some road base applications.
- Value-added use options for IGCC slags are practically feasible, but could to be limited, due to legislative, economical or technical barriers (e.g. absence of regulations, cost of transportation and processing, and absence of technical specifications, respectively).
- Where use is not feasible, slag is most commonly disposed of through mine backfill or landfill.
- To identify the suitability of IGCC slags for these and other potential applications in Australia, more research is required to fully understand their characteristics and how they vary with coal type and gasifier technology.

Preliminary assessment of available data

According to a preliminary assessment of published results from the characterisation of a small sample set of gasification slags produced from Australian coals, the slags would meet current requirements for landfill disposal. This is because the slags are non-leaching or low-leaching materials, which would likely be classified as a non-hazardous by-product. However, bulk analysis of by-products indicates that their classification can be significantly affected by the total concentration of specific trace elements. All analysed by-products have at least one element – chromium (Cr), molybdenum (Mo), nickel (Ni), lead (Pb) or selenium (Se) – at a concentration exceeding the lowest limits specified in current regulations. The relative importance the current regulations place on bulk chemistry, compared with the leachability of the species present, may complicate the characterisation of gasification slags in the absence of specific regulations for these materials.

The influence of feed coal characteristics and gasifier operation on trace element behaviour and concentration, and slag leaching behaviour, is largely unknown. This needs to be determined to ensure that the appropriate environmental and legislative requirements can be met.

Laboratory program

A preliminary laboratory program analysing the limited number of available gasification slag samples derived from Australian coals has begun to address some of the issues outlined in the review. The trace element concentrations and leachability of these samples were characterised using available leach tests. The behaviour of ‘real’ slags (produced from Australian coals in pilot & commercial gasifiers) was compared with that of slags produced from similar coals under laboratory conditions to investigate potential laboratory procedures that could assess the suitability of slags from specific coals for use or disposal.

Key results of the laboratory work are:

Assessment of slag compliance to regulatory standards

- Gasification slags from Australian coals are generally low-leaching materials, based on the commonly used Australian Standard Leaching Procedures (ASLP) and toxicity characteristic leaching procedure (TCLP) tests. Some samples, however, have results for specific elements that vary between the leaching tests used. Some of these results are sufficiently significant to lead to the potential for differences in assessment of disposal requirements in different states. Standardisation of leaching tests and the application of their results is required.
- Although the abundance of most trace elements in gasification by-products is similar to that observed in Australian coal combustion fly ashes, they have relatively higher contents of boron (B), Cr, Ni and tin (Sn). The total concentration of barium (Ba), cobalt (Co), Se and Ni – particularly in gasification fly ashes – may also exceed some of the lower limits specified in current (ash-related) regulations. In these cases, the classification would be affected more by the total concentration of trace elements than by the elements’ leachability.

Characteristics of laboratory-made slags and comparison with ‘real’ slags

- Most trace elements appear in laboratory-made slags in a manner consistent with their appearance in real slags; some trace elements’ species, however, are affected by the conditions of preparation, and so need to be considered with caution.
- Specific aspects of laboratory preparation therefore need to be accounted for to minimise the effects on such species.
- Leaching characteristics of slags are strongly dependent on conditions of slag formation, and (at least initially) access to real slags (e.g. from pilot-scale or industrial testing) from a specific coal are required to complete the environmental assessment of gasification by-products.

Characteristics of gasification slag from Australian coal for use in the cement industry

- Analysis showed that ground slag from gasification of an Australian coal is potentially useful as an additive in cementitious materials; however, due to its hardness, milling could be an expensive procedure.
- Intrinsic slag characteristics, such as hardness, and their dependence on coal properties and gasification conditions vary significantly between coals and gasifiers, and are not extensively studied. Further consideration and investigation is required to assess the general use of slags in the cement industry.
- Slag can potentially be used in alternative concrete binders, such as geopolymers.

Conclusions and further work

By-products from gasification of Australian coals have a range of disposal and use options, due to the generally inert nature of slags, and the general similarity of gasification-derived fly ash material to that obtained from pf applications. The most suitable strategy, however, will be affected by the comparable costs, including handling, processing and transportation, of their disposal and use; gasification site location, which includes infrastructure development and local state regulations; and current market needs. The outcomes of this work have demonstrated the importance of technology and coal-specific issues. These include by-product composition and physical properties, how by-products are likely to depend on feed coal properties and gasification conditions, and their subsequent disposal and use.

While IGCC or gasification by-products are not specifically mentioned in current Australian legislation, they are likely initially to be assessed in the same manner as coal combustion products, such as fly ash and bottom ash. While a more uniform, national approach is required to classify solid wastes, the current practice of primarily assessing options for the use of materials in the context of their source industry – rather than their physical and chemical properties – may pose a more significant challenge.

There are potential uncertainties associated with differences in the test procedures used to assess and classify waste materials. As different concentrations of trace elements are obtained in leachates when using different buffer solutions, the most appropriate leaching test procedure for a specific disposal or use scheme must be applied. The characteristics of the gasification by-product have to be assessed, as well as the environment in which they will be disposed or used. Current classification schemes are unable to make these distinctions.

The properties of slag that are assessed to determine their suitability for use in a range of industries vary significantly with coal type, and potentially, with gasification conditions. The lack of knowledge of slag characteristics and how they depend on these factors, however, narrows their potential fields of use for initial projects. We must gain a clearer understanding of these characteristics, which are affected by feedstock variety and are dependent on gasifier types and operational conditions. These considerations will provide a base for the development of standards and specifications for the use of slags and other gasification by-products as a raw material in industrial applications.

Part I **Review of Relevant Regulations and Legislation**

1 Introduction

Gasification technologies offer a pathway to achieve higher efficiencies and lower emissions than current coal combustion-based power generation technologies. Significant advances in cost, availability and reliability of integrated gasification combined cycle (IGCC) systems have been made in recent years as they make the transition from the chemical and refinery industries, where they are established commercial technologies, to the power sector. Gasification-based systems are also well suited to include staged, integrated carbon dioxide (CO₂) capture, and are currently used in commercial hydrogen production and syngas processing technologies. Next-generation IGCC plants will incorporate carbon capture technologies, further development of which will significantly reduce the cost and energy requirements of CO₂ capture.

Most of the current commercial and demonstration-scale IGCC-carbon capture and storage (CCS) projects are based on entrained flow gasification of coal. The first Australian commercial-scale coal gasification systems (likely to be the Perdaman project in Western Australia) will also use entrained flow gasification technology. These gasification technologies are designed to melt the mineral matter in coal and produce a liquid slag. The slag is quenched in the process, forming a glassy solid for storage, disposal or further use. Gasifier slag represents the vast majority of solid residue from entrained flow gasification systems. This high-density, glassy frit material is potentially a marketable by-product. Some of the coal mineral matter is also captured as fly ash (or fly slag) in the downstream gas and process water cleaning systems. Dissolved salts are removed from the process in the black water. As a result of process water treatment, chlorides, sulphides, cyanides, and heavy metals such as chromium, cadmium, or zinc can be included in this secondary solid waste stream.

Any Australian IGCC-CCS demonstration project will produce significant quantities of slag and other solid by-products. Australia currently has no coal gasification-based chemical or power plants. While coal gasification is widely used around the world, the use of coal-based IGCC for power generation internationally is currently limited to six commercial-scale plants. Research supporting the deployment of gasification-based systems for power generation has been driven in part by the significant differences between coal gasification and the well-understood process of coal combustion in a pf boiler, and how these differences affect fuel selection, process design and system optimisation. The permitting, licensing, and technical requirements for the storage, disposal, and handling of solid wastes from these new technologies are therefore uncertain. Data and knowledge of the properties of slags and other solid residues produced from entrained flow gasification of Australian coals are fundamental to addressing these uncertainties.

There is an expectation that slags produced by coal-fired gasifiers will be environmentally benign. If this is so, there should be no major issues related to the use or disposal of these materials, and they would not be expected to require special processing before transport and disposal under current disposal regulations (although more stringent future environmental regulations may make disposal more difficult). Recent work, however, has identified some trace element species that can leach from gasification-derived slags [1, 2]. Coal and process-specific issues may also affect the nature and extent of this leachability. Partitioning of some trace elements between slags and fly ashes is likely, but is dependent on coal properties and gasification conditions. Therefore, the leachability of the residues from specific coals needs to be understood to support decisions regarding slag use or disposal opportunities.

Most of the waste from the power industry in Australia is pf coal fly ash. This is stored in ash dams or disposed of as landfill: a practice currently under examination in the United States for environmental reasons. Disposal of fly ash in the United States is expected to become more costly and much more

tightly regulated. Considerable research is underway worldwide to minimise the environmental impacts of waste materials and to streamline waste disposal techniques to make them more affordable.

Australia has very limited industrial experience of handling and managing slags and solids from gasification. Some relevance is found, however, in slags produced in the steel industry. Experience with blast furnace and steelmaking slags has shown that these slags are regarded as valuable products, rather than waste; more than 95% of steelmaking slags are used.

While there is some international experience with gasification slags, the issues with gasification by-product disposal or use in Australia are complicated by the uncertainty associated with legislative and other requirements of gasifier operators regarding handling, disposal and use of gasification-derived solids. The international chemical industry has extensive experience with gasification-derived slags, but the limited experience with IGCC slags in the power sector – and the lack of local experience – is a challenge for the Australian power industry when making decisions about slag handling. This situation is compounded by the lack of data for the specific coals that will be used in any future Australian IGCC or IGCC-CCS demonstration and commercial projects.

Knowledge of the characteristics and environmental impacts of gasification slag and fly ashes is necessary to achieve high levels of use and to identify the sustainability of disposal strategies. This involves studying the composition of by-products and relating this to coal properties and gasifier operating conditions. It also involves knowledge of the leachability of potentially toxic or troublesome elements, as well as issues (such as physical and chemical properties needed for practical applications) that may affect the use of slag and fly ashes as valuable by-products.

This project begins the process of identifying and addressing the issues associated with slag disposal and use that are of direct relevance to Australian gasification projects using Australian coals under Australian technology and market conditions. As a first stage of the program, this review assesses the available data, experience, regulations and outcomes of slag management practices in existing international IGCC projects, international coal-gasification-based chemical industry practices, and in other relevant technologies such as iron and steel making. This information is presented in the context of current practices for management of solid wastes from existing coal combustion-based processes that are more familiar to the Australian power sector.

Sections 2 and 3 of the review focus on disposal options for gasification by-products in the context of regulations for the disposal of coal use by-products. Section 3 includes specific information regarding assessment of characteristics of different types of coal use by-products, including coal slags that have important use or disposal issues.

Sections 4 and 5 give overviews of disposal and use practices of ash, gasification slags, and slags from other relevant industries. Their relevance to handling of IGCC by-products in Australia (and in particular, Queensland), such as steelmaking slags, is discussed. Potential avenues for use of gasification by-products are discussed in Section 6, and the barriers to such use options are identified in Section 7. Section 8 summarises the findings of the review and provides recommendations for further work and issues to be resolved.

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2 Relevant legislation and regulations for by-product use and disposal

2.1 Introduction

One of the potential barriers to the use of gasification residues is that of legislation. Gasification residues may be classified as waste, and further subdivided, depending whether they are seen to be hazardous or non-hazardous. In this section, relevant Australian federal and state legislation is presented and compared with international legislation.

Although gasification is a mature technology in the chemical industry, its application to power generation is relatively new. No legislation relating specifically to this use appears to have been formulated. Regulations that may be applicable have been developed for coal combustion products (CCPs), which include fly ash, bottom ash, and boiler slag. Regulations on slag disposal or use usually refer to steelmaking slags. As gasification by-products consist of both fly ash and slag, it is most likely that, in the first instance, they would be addressed using existing legislation dealing with CCPs and steelmaking slags.

Information on legislation relevant to use and disposal of ash has been previously reviewed within the Cooperative Research Centre for Coal in Sustainable Development (CCSD) research program [1–4]. In many countries, ash from coal-fired stations is defined as a waste. The major portion of the ash is discarded in landfill, or in specially constructed ash dams. Following this approach – from an industry viewpoint – coal gasification slags are also likely to fall into the category of ‘waste’ rather than being seen as a ‘product’.

While gasification slags are expected to be more stable than ‘conventional’ fly-ash, the major concern likely to arise from the disposal and use of IGCC by-products is the potential leaching of environmentally hazardous trace elements. Relevant laboratory leaching procedures and other chemical characterisation tests are discussed in Section 3 of this review. This section gives an overview of relevant aspects of waste classification and management regulations, with a particular focus on Australian legislation.

2.2 Definition of waste and classification of gasification residues

2.2.1 BASEL CONVENTION

Wastes are defined internationally following the Basel convention to be ‘substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law’ [5].

The Basel Convention came into force in 1992 and, as at 1 January 2011, there were 175 parties to the convention. Australia signed the convention in 1991. It is implemented in Australia by the Hazardous Waste Regulation of Exports and Imports Act of 1989 and regulations of 1996.

Coal gasification and combustion by-products are defined (Basel Convention Annex I – categories of wastes to be controlled) to be hazardous wastes, as they include compounds of beryllium, hexavalent chromium, copper, zinc, arsenic, selenium, cadmium, antimony, tellurium, mercury, thallium, and lead—even though the concentrations of these elements in coal ash and coal slags are very low. These substances can be grouped according to two hazardous substances characteristic lists (Basel Convention Annex III – list of hazardous characteristics), specifically:

- exotoxic substances or wastes, which if released, present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems (UN Class 9, Code H12)
- capable, by any means, after disposal, of yielding another material, e.g., leachate, which possesses any of the Annex III characteristics i.e. flammable, toxic, poisonous, toxic, exotic (UN Class 9, Code H13).

The convention indicates that if compounds in the waste are listed in Annex I, and they possess any of the Annex III characteristics, then they are a hazardous waste. Following this, coal gasification by-products, which contain metallic compounds with the ability to form leachates, could be defined as a hazardous waste.

Unlike coal ash, coal slags are not specifically mentioned in the convention. However, Annex IX does mention metallurgical slags, which are not considered wastes unless they contain Annex I material to an extent causing them to cause an Annex III characteristic. Metallurgical slags that are not considered as wastes in Annex IX include:

- slags from copper processing for further processing or refining not containing arsenic, lead or cadmium to an extent that they exhibit Annex III hazard characteristics (B1100)
- granulated slag arising from the manufacture of iron and steel (B1200)
- slag arising from the manufacture of iron and steel including slags as a source of titanium dioxide (TiO₂) and vanadium (B1210)
- slag from zinc production, chemically stabilised, having a high iron content (above 20%) and processed according to industrial specifications (e.g. DIN 4301), mainly for construction (B1220).

Coal fly ash and most metallurgical slags are therefore defined to be a non-hazardous waste, unless it or its leachate contains Annex I substances (metallic compounds) at levels that cause them to exhibit Annex III characteristics.

2.2.2 THE ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

In 2004, further to the Basel Convention, the Organisation for Economic Co-operation and Development (OECD) Council produced the C(2004)100 recommendation on the Environmentally Sound Management (ESM) of Waste [6]. All waste, regardless of its classification as hazardous or non-hazardous (with the exclusion of radioactive waste), is covered by the recommendation. The main reason for the inclusion of hazardous and non-hazardous materials is the variation in hazardous waste testing procedures from one country to another. The application of ESM to 'waste in general' (i.e. independent of its potential as a hazard) ensures that all wastes (other than radioactive wastes), and including those that are difficult to characterise, are subject to the ESM recommendation.

Furthermore, the OECD Decision of the Council C(2001) 107/Final, concerning the control of trans-boundary movements of wastes destined for recovery operations, as amended by C(2004)20, specifies categories of waste subjected for recovery procedures. This list includes bottom ash, fly ash and slag tapped from coal-fired power plants and specifies the conditions for recovery:

- Wastes shall be destined for recovery operations within a recovery facility, which will recover the wastes in an environmentally sound manner according to national laws, regulations and practices to which the facility is subject.
- All persons involved in any contracts or arrangements for trans-boundary movements of wastes destined for recovery operations should have the appropriate legal status, in accordance with domestic legislation and regulations.

- Trans-boundary movements shall be carried out under the terms of applicable international transport agreements.
- Any transit of wastes through a non-member country shall be subject to international law and to all applicable national laws and regulations.

The OECD recommendation notes that: ‘Classification of waste according to its hazardous properties should be independent of local or regional conditions. The Basel Convention aims to control the trans-boundary movement of hazardous waste. Site-specific analysis is inappropriate in that context because the result would be different classification determinations at different sites for the same waste, which would be confusing at best. Therefore, the system of classification is based upon the principle of intrinsic hazard of the waste or its chemical constituents.’ [7].

2.3 European Union

The European Waste Catalogue (EWC) classifies waste materials according to their nature and how they were produced [8]. It uses the same terminology, principles and general intent of the Basel convention. The member states are fulfilling their requirement to integrate the catalogue into their domestic legislation.

The catalogue has been amended several times since the initial list of wastes was produced. According to the current version of the catalogue, Category 10 ‘Inorganic wastes from thermal processes’ and Sub-category 10.01 ‘Wastes from power stations and other combustion plants’ lists bottom ash, slag and boiler dust (10.01.01) and coal fly ash (10.01.02) as ‘non-hazardous’, unless they contain ‘dangerous substances’. Slags from the iron and steel industry are also classified under Category 10 as non-hazardous.

An important distinction that must be considered when assessing slags and ashes according to their origin is the nature of the chemical process concerned. For example, gasification slags are produced under strongly reducing conditions, and hence, the chemical species are significantly different from those found in combustion derived fly-ashes, which are formed under oxidising conditions.

The EWC contains two entries regarding steelmaking slag: waste from the processing of slag (10.02.01) and unprocessed slag (10.02.02). With regards to unprocessed slag, it is noticed [9] that, upon request of Germany, the EU-Commission agreed that granulation, pelletisation, foaming, proper solidification connected with a specified heat treatment, and separation, crushing, sieving, and milling are all examples of slag processing. If slag has undergone one or more of these processes, then it is not covered by the EWC and should not be classified as waste.

2.4 North America

2.4.1 FEDERAL REGULATIONS

In North America, solid waste regulations are outlined in the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act (RCRA)[10]. Regulated wastes are characterised as either hazardous (covered by RCRA Subtitle C) or non-hazardous (covered by RCRA Subtitle D) wastes with regulations specific to the waste type. Subtitle C of RCRA imposes requirements on the generation, transportation, storage, treatment and disposal of hazardous wastes, while non-hazardous wastes are subject to regulation by the states as solid waste. A significant policy issue affecting electric utilities that use coal has been the question of whether or not coal combustion products should be regulated at the federal level as hazardous wastes under Subtitle C [10].

A 1993 United States Environmental Protection Agency (US-EPA) final regulatory determination exempted coal use by-products (CUBs) from regulation as a hazardous waste under RCRA. The US-EPA currently applies this exemption to fly ash, bottom ash, slag and flue gas desulphurisation (FGD)

by-products that are managed independently of any other wastes [10]. The Energy and Environment Research Centre (EERC) 1999 Barriers Report noted that an important barrier originating in RCRA legislation is the indiscriminate designation of CUBs as solid wastes, whether they are recovered for use or disposed of in a regulated facility [11]. The 'waste' designation can generate case-by-case approval and permitting procedures that discourage the use of CCPs.

In 2000, a US-EPA regulatory determination concluded that CUBs that are co-managed with other wastes do not warrant regulation as hazardous wastes. It also concluded that no additional regulations are warranted for coal combustion wastes that are used beneficially, except for mine filling. However, the US-EPA also stated its intent to develop nationwide regulations for disposal of CUBs. Prior to this, all regulations governing CUB disposal and use had come from individual states [10]. In March 2011, the US-EPA finalised regulations in which coal fly ash, bottom ash and boiler slag were identified as 'Non-hazardous secondary materials that are solid waste coal combustion residuals' [11, 12].

The US-EPA is currently finalising standards and procedures to be used to identify whether non-hazardous secondary materials are solid wastes when used as fuels or ingredients in combustion units.

In their 'Advance Notice of Proposed Rulemaking', the US-EPA 'considered various guiding principles, including the concept of discard, and if discarded, whether the secondary material has been processed to produce a non-waste fuel or ingredient product, and the concept of legitimacy. For those secondary materials used as an ingredient, they should be handled as a valuable commodity, the secondary material provides a useful contribution, the recycling results in a valuable product, and the *product does not contain contaminants that are significantly higher in concentration than traditional products*. If these criteria are not met, then recycling may be indicated and the secondary material may be a solid waste' [12].

The US-EPA authorised most states to manage their own solid and hazardous waste generator regulatory program. Therefore, states may have their own set of regulations that apply in lieu of federal regulations. While most solid and hazardous waste state regulations are based on federal requirements, some states have developed regulations more stringent than the federal program. Requests for permission to beneficially use CUBs are frequently handled on a case-by-case basis or under generic state recycling regulations. States that do specify acceptable beneficial use applications for CCPs and CUBs are generally those that have made the most progress regarding CCP and CUB use in a manner that is technically feasible while protecting the environment [13].

2.4.2 SPECIFIC STATE REGULATIONS

An overview of state solid waste laws and regulations governing the beneficial use of CCPs in all fifty states can be found in Volume 2 of *Engineering and Environmental Specifications of State Agencies for Utilization and Disposal of Coal Combustion Products* [14]. Over the last few years, United States industrial groups have promoted the use of CCPs and removed barriers prohibiting use, such as the lack of regulations allowing the beneficial use of CCPs. Each state had an industry group whose membership consisted primarily of the state's electric generating companies. Examples of how these industry-led groups aided in developing beneficial use regulations in each of the states and descriptions of the resulting specifications have been published [15]. Information on state-level solid waste regulations for states that currently have a significant number of coal-fuelled electric generating units was also reported [15] and is summarised in Table 1.

Regarding CCPs disposal practice (as waste), potential environmental concerns from coal ash pertain to pollution from impoundment and landfills leaching into ground water, and structural failures of impoundments, such as occurred at the Tennessee Valley Authority's plant in Kingston, Tennessee. The need for national management criteria was emphasised by the December 2008 spill of CCPs

from a surface impoundment near Kingston. The spill flooded more than 300 acres of land with CCPs and flowed into the Emory and Clinch rivers.

None of the applicable solid waste discharge regulations appear to limit the introduction of IGCC technology any more than they limit coal combustion-based technology [10]. Forty-five states, encompassing 96% of the United States coal-fired utility generating capacity, duplicate the federal exemption of coal combustion by-products from being categorised as a hazardous waste. Since IGCC by-products have demonstrated better toxicity characteristics than wastes from coal combustion-based plants, IGCC should be no more affected than coal combustion-based plants. The US-EPA's proposed 'coal ash rule' does not apply to coal gasification slag/ash. It has a Bevill waste exemption from Subtitle C (hazardous wastes), as a 'mineral processing waste' [16].

State	Coal combustion product (CCP) and coal use by-product (CUB) regulations
Texas	Exempt from solid waste classification. No permits or prior approvals are required as long as the CCPs meet the eight-waste criteria rule. If CCPs are stored or disposed as wastes, the General Prohibitions apply along with other solid waste regulations.
Pennsylvania	Coal ash is excluded from the definition of solid waste and there are established provisions for its beneficial use. Beneficial use of coal ash is regulated under Pennsylvania's Residual Waste Management Regulations [17].
Florida	Waste management and disposal regulations concerning CCPs have been fully developed. No comparable regulation that concerns the beneficial use of CCPs. Proposed beneficial use projects are evaluated on a case-by-case basis.
Louisiana	Gasifier ash and process waste water resulting from coal gasification are specifically exempt from regulation as hazardous wastes, categorising this ash as solid waste resulting from the processing of ores and minerals [18]. Reuse of coal combustion by-products is not specially addressed, but beneficial-use permits for land application of any solid waste is required.
Indiana	Coal combustion wastes are exempt from solid or hazardous waste regulations if the waste is not included in the definition of hazardous wastes and meets the Federal exemption under 42 U.S.C.A. § 6921. Additional exemptions from solid waste regulations are also provided for specific beneficial uses.
Alabama	Exempt from regulation as hazardous waste. Also provisions for exemption from designation as industrial solid waste. No specific provisions for reuse.
Georgia	Followed by federal exemption of CUBs from hazardous designation. No specific provisions for reuse.
Illinois	Exempt from regulation as hazardous waste. Also provisions for exemption from designation as industrial solid waste. Illinois law specifically authorises reuse. Provides a distinction between coal combustion waste and coal combustion by-product with separate regulations for reuse.
Kentucky	Exempt from regulation as hazardous waste. Fly ash, bottom ash, and scrubber sludge from coal-fuelled electric generating units are classified as special waste. Kentucky specifically authorises reuse with certain provisions.
New York	Exempt from regulation as hazardous waste. New York regulations specifically include provisions for CUB reuse.
Ohio	Exempt from regulation as hazardous waste. Additionally, nontoxic fly ash, bottom ash and slag are regulated as exempt waste. The reuse of CUBs that are regulated as solid waste is not specifically authorised. However, the reuse of non-toxic exempt waste is authorised.
Tennessee	Exempt from regulation as hazardous waste. Fly ash, bottom ash, and boiler slag may be reused under 'permit by rule' regulation.
West Virginia	Exempt from regulation as hazardous waste. West Virginia includes specific provisions for the reuse and disposal of CUBs.

Table 1: Coal combustion products regulations in selected states of the United States

2.4.3 STEELMAKING SLAGS IN THE UNITED STATES

Regulations on use and disposal of slags from the steel industry have a longer history in the United States than those from coal combustion and gasification. Most of the states identify steelmaking slag as a valuable product, rather than a waste.

Under Pennsylvania's residual waste management regulations, steelmaking slag producers and processors have used determinations from the state Department of Environmental Protection (DEP) that their slag is a 'co-product' rather than a 'by-product' or 'waste' subject to regulation when used in place of natural aggregate in certain applications [19]. Slag producers and processors are required to demonstrate a rough equivalency in terms of chemical consistency and performance between the proposed co-product and the natural aggregate that it would replace.

Michigan regulations provide a simple exclusion for slag from its definition of solid waste. The statute's definition of solid waste does not include 'slag or slag products directed to a slag processor or to a re-user of slag or slag products' [20]. Slag is defined as 'the non-metallic product resulting from melting or smelting operations for iron or steel.' Following this definition, slag may be used in a variety of industrial, construction, or agricultural applications without the need to comply with extensive administrative requirements or regulations.

Ohio excludes 'slag and other substances that are not harmful or, inimical to public health' from the definition of solid waste [21]. The Ohio EPA has established an 'interim policy' that encourages the use of blast furnace slag in asphalt and concrete [22]. It notes that blast furnace slag generally does not present environmental issues when used as a construction material. However, slag should meet certain analytical requirements if used in aquatic environments with poor drainage. The Ohio EPA environmental regulations also require dust control and storm water runoff in the processing, stockpiling and storage of blast furnace slag.

In Indiana's solid waste land disposal regulations, steelmaking slag is specified as a solid waste resulting from iron and steel manufacturing or foundries under the definition of 'industrial process waste' [23]. However, steelmaking slag is exempted from these regulations if the use is 'legitimate.' Specified legitimate uses include 'use as a base for road building.'

Illinois regulations also exempt certain uses of steelmaking slag from its requirements for steel industry wastes [24]. For land reclamation purposes, steelmaking slag may be used provided that such use will not exceed of applicable groundwater standards. Uses of steelmaking slag that are not exempt under the above provisions must meet the maximum allowable leaching concentrations based on federal National Primary and Secondary Drinking Water Standards. If these standards are met, the steelmaking slag may then be used as a substitute for commercially available materials.

2.5 South Africa

In South Africa, waste is defined as 'an undesirable or superfluous by-product, emission, or residue of any process or activity which has been discarded, accumulated or stored for the purpose of discarding or processing. It may be gaseous, liquid or solid or any combination thereof and may originate from a residential, commercial or industrial area'. This definition excludes industrial waste water, sewage, radioactive substances, mining, metallurgical and power generation waste [25].

First drafts of some new regulations in the revised Waste Classification & Management System were recently developed (2010, [26]) including:

- National Waste Classification and Management Regulations
- National Standard for Leach Tests and Screening Values for Risk Profiling of Waste
- National Standard for Disposal of Waste to Landfill.

According to the revised system, waste can be classified as Excluded Waste and Pre-classified Waste, which includes categories of Hazardous waste and General Waste. Fly ash and dust from miscellaneous filter sources, bottom ash and slag are classified as a General Waste. Once the system has been finalised and formalised into regulations in terms of the Waste Act, the Chemical and Allied Industries' Association will develop guidelines for industry [26].

2.6 Asia

In China, fly ash and slag are classified as a solid waste. Power plants use the classification of fly ash for disposal and to sell for industrial applications. Currently, there is no classification for slag in gasification plants, and it is believed that no specific regulations are used for handling, transportation and use of the slag. Slag and fly ash from gasification plants are mainly used for cement production. No standard leaching tests are applied to slag disposal [27].

The Japanese national government place much emphasis on the need for recycling and minimising waste. No specific Japanese legislation on the disposal of coal combustion and gasification by-products has been identified [28]. More than 80% of ash from coal power station in Japan is used, and it is likely specific legislation is regarded as unnecessary. Although there are no specific national laws on CCP disposal, some section of the Basic Environment Law of Japan [29] relate to disposal of wastes, including CCP. The Law for the Promotion of Utilisation of recyclable resources refers to use of specific materials, including coal ash generated by the electricity industry [30].

2.7 Australia

2.7.1 FEDERAL LEGISLATION

In November 2008, Australia's environment ministers agreed to prepare the first comprehensive national report on resource recovery and waste management. Just before this, the Senate report *Management of Australian Waste Streams* concluded that Australia lacks fundamental information on most aspects of waste generation and management, including physical, financial, economic and social aspects, and needs adequate tools to process such information.

In November 2009, the Environment Protection and Heritage Council (EPHC) released the *National Waste Policy: Less Waste, More Resources*. The policy sets out a comprehensive agenda for national, coordinated action on waste. It identifies strategies that are designed to:

- provide a coherent, comprehensive national framework for waste management, resource recovery and the avoidance of waste over the next decade
- enable Australia to meet its international obligations in regard to management of hazardous wastes and substances into the future and reduce the risk and improve the legacy for future generations
- address marked impediments and streamline regulatory frameworks so that national companies and small businesses can operate effectively, and manage products and materials responsibly, during and at end of life
- provide national leadership on waste and resource recovery where it is needed and facilitate collaboration between states on national issues
- contribute to climate change, sustainability, innovation and employment opportunities
- be of high impact and cost effective by setting clear national directions and through collaborative, carefully targeted action that incrementally builds on the existing efforts of governments over a ten-year period.

In July 2010, the EPHC endorsed the National Waste Policy Implementation Plan, one objective of which was the 'introduction of a national definition and classification system for waste that aligns with definitions in international conventions due in the middle of 2011'.

The *Hazardous Waste Act 1989* implements the Basel Convention and primarily deals with the movement of hazardous waste. If a substance is defined as a waste, the next steps is to determine if it is hazardous as defined by the Basel Convention; and, if so, determine the appropriate protocols to apply, which are provided by the National Environment Protection Measure. Although IGCC residues are unlikely to be classified as hazardous, some of their metal components, such as selenium and chromium, are hazardous; they are potentially ecotoxic, poisonous or capable of forming leachates. The toxicity characteristic leaching procedure (TCLP) is used to determine if a threshold concentration is exceeded, in which case the material is hazardous with respect to that metal.

The Environment Protection and Heritage Council/National Environment Protection Council

The EPHC was established in 2001 by the Council of Australian Governments and incorporates the National Environment Protection Council. The EPHC has a broad role in environmental protection and development of relevant environmental policy. One such responsibility is the movement of waste between states and territories, which falls under the National Environment Protection Measure. This policy covers the movement of waste solely within Australia. It defines waste as either 'any discarded, rejected, unwanted abandoned or surplus matter', or 'otherwise discarded, rejected, unwanted abandoned or surplus matter which is intended for recycling, reprocessing, recovery, reuse or purification by an operation separate from that which produced the matter or is offered for sale'.

Recently, the Environmental Protection Authority (EPA) has stipulated a Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption under Part 6, Clause 51 and 51A. This is the coal ash exemption 2011, effective as at 14 June 2011 [31]. These clauses authorise:

- the EPA to grant an exemption in relation to any matter or thing, including an activity or class of activities
- the EPA to exempt a person from any of the provisions in relation to an activity or class of activities relating to certain waste that is to be land applied or used as a fuel
- the provisions of Sections 47 to 49 and 88 to the *Protection of the Environment Operations Act 1997* (the Act)
- the provisions of Schedule 1 to the Act, either in total or as they apply to a particular activity
- the provisions of Part 3 and clauses 45 and 47 of the Regulation.

In the notice of exemption (effective as at 14 June 2011):

- The responsible person listed in Column 1 of Table 2 is exempt from the provision/s listed in Column 2 of that table, but only in relation to activities involving the relevant waste and only where the responsible persons comply with the conditions as set out in Column 3. This notice does not exempt the responsible person from the provisions as described in Column 2 where the relevant waste is received at premises that are, despite this exemption, required to be licensed for waste disposal under the provisions of the Act.
- Where a responsible person complies with the conditions of this Notice of Exemption, the activity referred to in Schedule 1 from which that person is exempt is taken to be a non-scheduled activity for the purposes of the Act.

Column 1	Column 2	Column 3
Responsible person	Provisions from which the responsible person is exempt	Conditions to be met by the responsible person
Generator	Section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation	All requirements specified in Section 7 and 8
Processor	Section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation	All requirements specified in Section 7 and 9
Consumer	Section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation Section 88 of the Act Clause 47 of the Regulation	All requirements specified in Section 7 and 10

Table 2: Responsibility in coal ash exemption as per the Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption

General conditions of the exemption as per the Notice of Exemption are as follows:

- Concentrations of chemical elements in the coal ash as listed in Column 1 of Table 3 must not exceed the following:
 - the absolute maximum concentration or other value listed in Column 4 of Table 3
 - for characterisation or one-off tests, the maximum average (as based upon the arithmetic mean) concentration or other value listed in Column 2 of Table 3
 - for routine tests, the maximum average (as based upon the arithmetic mean) concentration or other value listed in Column 3 of Table 3.
- The coal ash can only be applied to land as an engineered fill, stabiliser, filter or drainage material or as a sand substitute as follows:
 - pipe bedding material
 - selected backfill adjacent to structures
 - composite filler in asphalt pavements
 - road pavement, base and sub-base structures
 - rigid and composite pavement structures
 - select layers that act as working platforms at the top of earthworks
 - fill for reinforced soil structures (including geo-grid applications).
- The coal ash can only be applied to land where:
 - it complies with a relevant specification or Australian Standard or supply agreement/s
 - planning or development consent that has specifically considered the use of coal ash has been granted for the project.
- The coal ash can be applied to land when blended with other exempted materials, provided the blended materials have been validated as compliant with the conditions of each individual exemption, for the use specified in each exemption.

Column 1	Column 2	Column 3	Column 4
Chemicals and other attributes	Maximum average concentration for characterisation	Maximum average concentration for routine testing	Absolute maximum concentration
Mercury	0.5	NR	1
Cadmium	0.5	0.5	1
Lead	25	25	50
Arsenic	10	NR	20
Boron	75	NR	150
Chromium (total)	25	25	50
Copper	20	NR	40
Molybdenum	10	NR	20
Nickel	25	25	50
Selenium	10	10	20
Zinc	35	35	70
pH range	7–12.5	7–12.5	6–13

Table 3: Acceptable values of chemical concentrations (mg/kg) and pH for coal ash exemption, as per the Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption. NR, not reported.

This Notice of Exemption only applies to coal ash sampled according to the specified requirements.

Test methods shall be undertaken by analytical laboratories accredited by the National Association of Testing Authorities, or equivalent. All chemicals and other attributes listed in Column 1 of Table 3 shall be measured in accordance with the specified methods.

Ash generators must be responsible for sampling (according to AS 1141 methods), routine sampling according to the requirements listed in Column 1 and 2 of Table 3, characterisation and recording, and provide this information with a written statement of compliance to the processor or consumer.

Processor responsibilities include recording of the quality and proposed use of coal ash, and providing a written statement of compliance and latest characterisation test results to the consumer to ensure that the relevant waste is used in applications that are consistent with the conditions of this exemption.

The consumer is responsible for all records of the quantity and use of the coal ash received. The consumer must ensure that the coal ash shall not be applied in or beneath water, including ground water. The consumer should note that regardless of having an exemption, the use of coal ash remains subject to ALL other relevant environmental regulations within the Act and Regulations, including but not limited to land pollution and water pollution.

2.7.2 NEW SOUTH WALES

New South Wales' classifications are focused on the disposal options for specific wastes and incorporate a risk-based approach.

The waste regulations are administered under the principal legislation of the *Protection of the Environment Operations Act (POEO Act, 1997 as amended in 2008)* and the *Waste Avoidance and Resource Recovery Act (WARR Act) 2001*. New guidelines were included in the 2008 amendment [33] to support the waste classification system. These help waste generators classify waste to ensure its appropriate management, transport and disposal.

Wastes are classified into groups that have similar risks to the environment and human health. These groups (classes) include:

- special waste
- liquid waste
- hazardous waste
- restricted solid waste
- general solid waste (putrescible)
- general solid waste (non-putrescible).

Waste generators should chemically assess their waste to determine its classification where:

- the waste is not special waste, liquid waste, a waste classified by the EPA or a waste possessing hazardous characteristics
- the composition of the waste is not known.

As in the Australian Capital Territory, New South Wales regulations address the chemical assessment process. This is based around the waste's potential to release chemical contaminants into the environment through contact with liquids (mainly water), which leads to the production of leachates [33].

Where a waste producer does not wish to undertake this assessment, the waste must be managed as if it were hazardous waste. Hazardous waste cannot be disposed of directly and must be treated.

Coal falls under the waste legislation and 'ash' is noted under the Protection of the Environment Operations Act, 1997 [34]. This Act specifies that sites that receive in excess of 20,000 tons and store ash from electricity generation plants are not classified as waste facilities. As such, the ash, which is non-hazardous, is not deemed to be waste [35].

2.7.3 AUSTRALIAN CAPITAL TERRITORY

The Australian Capital Territory's waste classification is based on the risk-based approach previously used by New South Wales, where types of non-liquid waste include:

- hazardous
- industrial
- solid
- inert.

Coal ash and slags are not listed in for particular types. This means that they have to be assessed through the classification process for non-liquids, which focuses on the potential for the waste to release chemical contaminants into the environment through contact with liquids (i.e. leachates). Details of the assessment process are given in Technical Appendix 1 [32].

2.7.4 QUEENSLAND

The primary approach in Queensland's classifications is to drive wastes toward specific treatment routes. There are three waste classification types:

- General Waste
- Limited Regulated Waste
- Regulated Waste (includes commercial and industrial waste).

Queensland's legislation promotes treatment of Regulated Waste (similar to the approach for Prescribed Industrial Waste in Victoria) to become Limited Regulated waste. This is lower in toxicity than Regulated Waste and less expensive to dispose of, as it can be disposed at General Waste landfills [38]. Limited Regulated Waste also does not require a Regulated Waste transport license, which again makes the waste less expensive to manage. Regulated wastes are reported separately.

A detailed analysis of current regulations and practice regarding fly ash disposal and use has been undertaken as part of this review. Key outcomes relevant to Queensland are indicated below:

- Fly ash is listed as a Regulated Waste in the Environmental Protection Regulation, 1998 [35]. However, there is an exemption published and enforced by the EPA, which states that:

‘Under the Provisions of the Environmental Protection (Waste Management) Regulation 2000 this approval of resource for beneficial use is issued to: the Ash Development Association of Australia ...’ [39].
- The conditions of this exemption are detailed in Schedule A of the Notice of Decision issued by the EPA. This approval, however, is only applicable to the Ash Development Association of Australia and its members, with effect from the 30 November 2007 [39].
- This approval for CCPs is limited to
 - pipe bedding materials
 - sub surface drainage
 - selected backfill adjacent to structures
 - road pavement, base and sub-base structures
 - binder for road stabilisation pavements
 - composite filler in asphalt pavements
 - rigid and composite pavement structures
 - select layers that act as working platforms at the top of earthworks
 - fill for reinforced soil structures (including geo-grid applications).
- Another exemption was introduced in 2010. This Notice was the General Approval of a resource for beneficial use – Coal Combustion Products used in Bound Final Products. This exemption allows relevant persons to use CCPs in manufacturing processes and applications that encapsulate or chemically transform and incorporate the resource into a final product. Final products for the purpose of this approval are limited to
 - cementitious mixes
 - cement products
 - concrete products
 - ceramic products
 - asphalt
 - insulation
 - paints
 - plastics
 - geopolymers
 - rubbers.

This approval only applies where there is a generator and an agreed user [40].

The Queensland Waste Strategy *Let's not Waste our Future* discussion paper of 2007 quotes the Environmental Protection Act of 1994. This defines waste as 'anything, other than an approved resource that is left over, or an unwanted by-product, from an industrial, commercial, domestic or other activity, or surplus to the industrial, commercial or domestic or other activity generating the waste'. It goes on to say that the waste can be a gas, liquid, solid or energy, or a combination of these, whether or not it is of value. The EPA may approve specified wastes as resources if those wastes are considered to have a beneficial use other than disposal.

In 2009, the Ash Development Association of Australia issued a report of its Coal Combustion Product Program [41]. The report outlines the association's 10-year effort to seek approval for CCPs as a resource for beneficial use. This application was approved and given effect by the Queensland state government from December 2007. The association conducted extensive analysis and investigations into the elemental concentration and leachability of selected metal species from coal combustion products using US-EPA, Department of Energy and Climate Change and Queensland EPA total and TCLP leaching tests [42].

The Queensland state government introduced a levy on industrial waste disposal, effective from the 1 December 2011. The proposed industry levy for low and higher-hazard regulated waste has been set at AU\$50 and \$150 per tonne, respectively. However, as mentioned earlier in this section, CCPs have been granted an exemption and are classified as a 'resource for beneficial use'.

2.7.5 SOUTH AUSTRALIA

South Australia waste classifications are applied to direct the following classes of wastes:

- municipal solid waste
- commercial and industrial (listed and general)
- construction and demolition (inert and mixed)
- listed waste.

Other key waste definitions include solid, liquid, inert, waste soil, medical, asbestos, asbestos containing material, radioactive, E-waste and quarantine.

Guidelines for solid waste, including criteria for assessment, classification and disposal, are currently under development. Information sheets provide the current criteria for the classification of waste as they appear on EPA licences, including Industrial and Commercial Waste (Listed) and Waste Soil [43]. Key waste definitions were updated in September 2009 [44]. Materials with hazardous characteristics are classified as hazardous waste and may not be sent to landfill. There are no specific definitions for coal ash and other CCP by-products in South Australia's classifications.

2.7.6 TASMANIA

The Tasmanian classification scheme is used mainly for landfill permit reporting requirements and for charging landfill fees. The state does not have a state-based waste levy.

Tasmania's *Landfill Sustainability Guide 2004* provides guidance on several key subcategories of waste [45]. Solid wastes are classified into municipal, commercial and industrial, and construction and demolition wastes. Hazardous waste is referred to as a controlled waste. Inert waste is a waste that will not degrade in the short term, and that has a negligible risk to the environment. There are no specific definitions for coal ash and other CCP by-products in the Tasmanian classification scheme.

2.7.7 VICTORIA

Victoria's legislation is primarily focused on prescribed industrial waste. When disposed in landfill, this waste must be categorised into one of three hazard categories: A, B or C [46]:

- Category A: Prescribed industrial wastes that require a very high level of control and ongoing management to protect human health and the environment. Wastes in this category cannot be accepted at a disposal facility without prior treatment to reduce or control the hazard.
- Category B: Prescribed industrial wastes that require a high level of control and ongoing management to protect human health and the environment. Solid prescribed industrial wastes in this category can be accepted at a facility licensed by EPA to receive this category of waste.
- Category C: Prescribed industrial wastes that pose a low hazard, but require control and/or ongoing management to protect human health and the environment. Solid prescribed industrial wastes in this category are able to be accepted at best-practice municipal landfills licensed by EPA to accept such waste.

Industrial wastes (not prescribed) are not regulated as prescribed industrial wastes, but when disposed of to landfill, continue to be controlled by EPA. These wastes can be accepted at solid inert landfills (non-putrescible) or municipal solid waste landfills (putrescible) licensed by EPA to accept this type of waste [47].

2.7.8 WESTERN AUSTRALIA

Western Australia's legislation is focused more on a management-based approach rather than the risk-based approach common in other states legislation, although the classifications also have risk-based elements. The primary approach is to identify the type of landfill suitable for disposal of specific classes of waste, rather than on differentiation of waste streams [38].

The *Waste Avoidance and Resource Recovery Act 2007* [48] defines waste as matter whether useful or useless, which is discharged into the environment; or, matter that is prescribed by the regulations to be waste. Following are the criteria to be applied in determining classification of wastes for acceptance to landfills licensed or registered in Western Australia:

- Inert landfill (Class I)
- Putrescible landfill (Class II)
- Putrescible landfill (Class III)
- Secure landfill (Class IV)
- Intractable landfill (Class V).

Each class, except for Class V, has six potential classifications. Intractable waste, which cannot be treated to a lower level of toxicity or made easier to manage, cannot be disposed of into landfill.

Section 3 of this review provides slag characteristics addressing their classification in different Australian states.

2.8 Criteria used for waste classification

A more detailed description of the analytical procedures used to characterise IGCC residues will be given in Section 3. The following is a brief description of how the tests are applied to classify waste materials in general.

2.8.1 DIFFERENCES IN CLASSIFICATION ROUTES

Procedures used to classify wastes differ among Australian states.

In New South Wales, the Australian Capital Territory, and Western Australia, the first stage of waste assessment includes assessing the total concentration of each trace element as specified in the regulations. Leaching tests are not required if the element concentration does not exceed the limit. If it does, then classification of the waste depends on both the specific element concentration and the leachable concentration. Consistently in those regulations, the limits for trace element concentrations increase from the limits where leaching test are not required, to the limits applied for restricted wastes.

In the Australian Capital Territory and Western Australian regulations, however, the same limits of trace element concentrations can be applied for different classes of wastes (e.g. inert and solid waste in the Australian Capital Territory classification) that require leaching tests. Further differentiation in the classification is based on the trace element concentrations in the leachates only.

In Victoria and South Australia, the route used for evaluation of trace element concentrations and leaching characteristics does not include trace element limits where a leaching test is not required: both trace element concentrations and trace element concentrations in leachates are used for classification of the waste. In the Victorian regulations, trace element limits are the same for less hazardous wastes (industrial and Category C), and their differentiation is based on the concentration limits in leachates. In South Australia, the limits of trace elements in wastes are the same for most elements and, as in Victoria, the differentiation in waste classification is only based on the concentration limits in leachates.

The Australian Capital Territory, New South Wales and Western Australia use two analytical tests to complete the assessment of waste: the Specific Contaminant Concentration (SCC) test and the Toxicity Characteristics Leaching Procedure (TCLP) or Australian Standard Leaching Procedure (ASLP).

- The SCC test determines the *total concentration* of each contaminant in the waste sample. The standards set different maximum levels for the total concentration of each contaminant to classify the waste. Results of the tests may be used directly in waste classification. If the trace element concentrations for each element (or compound) do not exceed a certain level (known as the Concentration Limit, or Concentration Threshold), further leaching tests (TCLP or ASLP) are not required. If it exceeds this level, classification of the waste is also based on the leaching characteristics (leachability) of the waste.
- The TCLP and ASLP estimate the potential for the waste to release chemical contaminants into a leaching liquid. The differences between these tests are discussed in Section 3. The standards set different maximum levels for the *leachable concentration* of each contaminant to classify the waste.

Both the ASLP/TCLP and SCC criteria must be satisfied before a waste can be classified as non-hazardous (inert, solid, industrial, putrescibles, etc.) unless the *immobilisation* of each contaminant exceeding the *total concentration* limits is approved by the EMA. If the level exceeds the highest ASLP/TCLP limits, the waste is classified as *Hazardous* (in the Australian Capital Territory and New South Wales); *Intractable* (in Western Australia); or *Category A – Prescribed Industrial* (in Victoria). The waste then has to be treated before disposal to reduce contaminant concentration to an acceptable level.

The regulations recommend the following procedures for leachate preparation [42]:

- AS 4439.1–1999: Wastes, Sediments and Contaminated Soils – Preparation of Leachates, *Preliminary Assessment* (Australian Standard 1999b)

- AS 4439.2–1997: Wastes, Sediments and Contaminated Soils – Preparation of Leachates, Bottle Leaching Procedure (Australian Standard 1997a)
- AS 4439.3–1997: Wastes, Sediments and Contaminated Soils – Preparation of Leachates, Zero Headspace Procedure (Australian Standard 1997b).

Table 4 lists the classes of wastes as used in Australian states, the test applied for characterisation, and the parameters used for classification.

Although state legislation and regulations may appear to use the same terminology, the threshold values used to classify the waste may vary because of the definitions used in a particular state or territory. For example, in the Australian Capital Territory regulations, the specific contamination and toxicity characteristic leaching procedures Level 1 values are lower than the equivalent values used in New South Wales, because the Australian Capital Territory has an additional category of ‘inert waste’. Furthermore, in the Australian Capital Territory regulations, the Level 3 and 2 values of the specific contamination concentration and toxicity characteristics leaching procedure levels correspond to Level 1 and 2 values in the New South Wales regulations.

2.8.2 VARIATIONS IN CRITERIA SPECIES ACROSS AUSTRALIAN STATES

Apart from differences in assessment procedures as indicated in Table 5, state regulations also differ in the elements listed for total concentration limits and leaching tests. Western Australia extends the list used by New South Wales and the Australian Capital Territory by adding total concentrations of metals, which include aluminium, barium, boron, cobalt, copper, manganese, vanadium and zinc. Victorian regulations are the same as those of the Australian Capital Territory and New South Wales, but also add antimony, barium, boron, copper, zinc and chloride limits.

The list of elements given in the South Australian regulations is very different from that of the other states. Perhaps surprising is the appearance of trivalent chromium: all other states include hexavalent chromium, which is known to be hazardous, while trivalent chromium is an essential nutrient and is not listed in most international conventions. South Australian regulations are in the development stage, however, and the list of elements is likely to be subject to change.

Concentration limits of selected elements used for waste classification in different states (associated with coal use by-products) are listed in Appendix B.

2.9 Conclusions

Gasification or IGCC by-products are not specifically mentioned in current Australian legislation. Despite the significant chemical and physical differences between CCPs and gasification slags, it is likely that gasification slags will initially be assessed in the same manner as CCPs, such as fly ash and bottom ash from coal-based combustion systems. If so, then they will most likely be classified as a waste, rather than a resource. However, as in the case of coal ash, there do not appear to be any specific legislative barriers to reuse. There is also a move away from a prescriptive approach to a ‘fit for purpose’ approach, although this is in its very early stages (e.g. recent Queensland legislation). It is also apparent that much of the current legislation is based more on international legislation than on Australian legislation. As shown in this section, Australian state legislation varies considerably. A more uniform, national approach based upon sound scientific information is required.

State or territory	Year	Classification	Methods/parameters	Limits/comments
ACT	2000	Inert	1.SCC 2.TCLP	1)<CT1; 2) <SCC1, <TCLP1; 3)<SCC1, <TCLP1*
		Solid		1)<CT2; 2) <SCC2,>TCLP1,<TCLP2, 3) >SCC2,>TCLP1,<TCLP2*
		Industrial		1)<CT3; 2) <SCC3,>TCLP2,<TCLP3, 3) >SCC2, <SCC3, ,<TCLP3, 4) >SCC3,>TCLP2,<TCLP3*
		Hazardous		1) >TCLP3 2) >SCC3,< TCLP3**
NSW	2008	General solid	1.SCC 2.TCLP	1)<CT1 2)>CT1,<SCC1, <TCLP1
		Restricted solid		1) <CT2; 2) >CT2, <SCC2, <TCLP2
		Hazardous		>CT2, >SCC2, >TCLP2
Western Australia	2009	Inert (Class I)	1.CL/CT 2. ASLP	1)<CT1 2)>CT1,<CL1, <ASLP1 3) >CL1, <ASLP1*
		Putrescible (Class II)		1) <CT2; 2) >CT2, <CL2, <ASLP2 3) >CL2, <ASLP2*
		Putrescible(Class III)		1) <CT3; 2) >CT3, <CL3, <ASLP3 3) >CL3, <ASLP3*
		Secure (Class IV)		1) <CT4; 2) >CT4, <CL4, <ASLP4 3) >CL4, <ASLP4*
		Intractable (Class V)		1)>ASLP4; 2)>CL4, <ASLP4**
South Australia	2010	Level 1 (former Intermediate)	1.TC 2. ASLP	<TC1, < ASLP1 (refer to General Solid (New South Wales)
		Level 2 (former Low Level Contaminated)		<TC2, <ASLP2
Victoria	2009	Industrial waste Category C – prescribed Industrial Category B – prescribed Industrial Category A – prescribed Industrial	1. TC 2.ASLP	<TC0, <ASLP0 <TC1, <ASLP1 <TC2, <ASLP2 >TC2, >ASLP2
Queensland	2011	General Limited Regulated Regulated	1. SCC 2. TCLP	<SCC, <TCLP***

Table 4: Classification of waste and applied parameters in Australian states and territories. ASLP, Australian Standard Leaching Procedures; CL, concentration limit; CT, Concentration Threshold; SCC, Specific contaminant concentration; TC, total concentration; TCLP, Toxicity Characteristics Leaching Procedures. *immobilisation is EMA-approved; **immobilisation is not EMA-approved; *for classification as resource for beneficial reuse**

	New South Wales	Victoria	Australian Capital Territory	Western Australia	South Australia	Queensland	Coal ash exemption
Antimony		v					
Arsenic	v	v	v	v	v	v	v
Barium		v			v	v	
Beryllium	v	v	v	v	v	v	
Boron		v					v
Cadmium	v	v	v	v	v	v	v
Chromium (III)					v		v
Chromium (VI)	v	v	v	v		v	v
Cobalt					v	v	
Copper		v			v	v	v
Fluoride	v	v	v	v			
Lead	v	v	v	v	v	v	v
Manganese					v	v	
Mercury	v	v	v	v	v	v	v
Molybdenum	v	v	v	v			v
Nickel	v	v	v	v	v	v	v
Selenium	v	v	v	v		v	v
Silver	v	v	v	v	v	v	
Zinc		v			v	v	v
Chloride		v					
Total other metals (Aluminium , barium, boron, cobalt, copper, manganese, vanadium and zinc)				v			

Table 5: Elements specified in Australian state regulations and in national coal ash exemption

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3 Characterisation of by-products for environmental assessment

3.1 Toxic species in coal use by-products

As discussed in Section 2, the classification of particular waste materials depends on their chemical characteristics. Usually, the primary concern associated with disposal or use of CCPs is the potential for ground water contamination. Toxic trace elements specified in most environmental regulations include arsenic, barium, cadmium, chromium, lead, mercury and selenium. The toxicity of these trace elements is summarised in Table 6 [1].

3.2 Techniques for characterising coal combustion products and other solid wastes

The chemical characterisation of CCPs is based on the total concentration of primary constituents of concern, and the leachability of these elements in aqueous media. Leachability characterisation focuses on chemical analyses of the leachates produced from CCP materials.

There are three types of leaching methods [2]:

1. Regulatory: those promulgated and approved by a regulatory agency to generate specific information for submission in a legal context
2. Standard: those adopted by a standards organisation (e.g. American Society for Testing and Materials [ASTM], International Organization for Standardization) for a specific set of conditions and sometimes for specific materials
3. Research: those developed for a particular research and development objective.

Some methods are intended to simulate environmental conditions, or to obtain specific information about the nature of the extractable material within a particular solid. The methods vary in the mass and particle size of the sample, the type and volume of leachant solution, the leachant delivery method and the leaching time. Most procedures are performed at ambient temperature, although some methods decrease the time required to dissolve components by increasing the temperature. Many of the leaching methods were developed for characterisation of municipal solid waste and industrial wastes; however, they have been applied to a variety of materials, including coal use by-products [3]. The common primary analyses used for regulatory purposes are the Toxicity Characteristic Leaching Procedure (TCLP) and extraction procedure (EP) analysis; details of these and other techniques are given below.

3.2.1 EXTRACTION PROCEDURE

The EP method was developed to determine the hazardous classification of a solid waste based on 14 specific organic and inorganic constituents designated in the United States Federal Register (1980). According to the relevant United States legislation, a solid waste exhibits the characteristic of 'EP toxicity' if the extract from EP, or any other approved test of a similar kind, contains any of the listed contaminants at a concentration equal to or greater than the specified value.

The EP [4] is performed by adding a specified quantity of water to a representative sample of the residue. The pH is then measured upon agitation. If the pH of the solution is higher than 5.0, it is adjusted to 5.0 ± 0.2 by adding 0.5 N acetic acid. Continuous pH monitoring and adjustment is carried out throughout the test to eliminate any effects arising from pH variations.

Element	Hazard and consequences
Antimony	Exposure to antimony occurs in the workplace or from skin contact with soil at hazardous waste sites. Breathing high levels of antimony for a long time can irritate the eyes and lungs, and can cause problems with the lungs, heart and stomach.
Arsenic	Exposure to higher than average levels of arsenic occur mostly in the workplace, near hazardous waste sites, or in areas with high natural levels. At high levels, inorganic arsenic can cause death. Exposure to lower levels for a long time can cause a discoloration of the skin and the appearance of small corns or warts. Ingestion of arsenic has been shown to cause skin cancer and cancer in the liver, bladder and lungs.
Barium	Barium has been found to potentially cause gastrointestinal disturbances and muscular weaknesses when people are exposed to it at levels above the EPA drinking water standards for relatively short periods of time.
Beryllium	Beryllium can be harmful if you breathe it in. High-level beryllium in air causes symptoms resembling pneumonia and is called acute beryllium disease.
Cadmium	The general population is exposed by breathing cigarette smoke or eating cadmium-contaminated foods. Cadmium damages the kidneys, lungs and bones. Cadmium and lead have the following effects: kidney disease, lung disease, fragile bone, decreased nervous system function, high blood pressure and anaemia.
Hexavalent chromium	Exposure to chromium occurs from ingesting contaminated food or drinking water, or breathing contaminated workplace air. Chromium (VI) at high levels can damage the nose and cause cancer. Ingesting high levels of chromium (VI) may result in anaemia or damage to the stomach or intestines.
Lead	Exposure to lead can occur from breathing workplace air or dust, eating contaminated foods or drinking contaminated water. Lead can damage the nervous system, kidneys and reproductive system.
Mercury	Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys and developing foetus.
Nickel	Skin effects are the most common in people who are sensitive to nickel. Breathing high Ni-contaminated air causes chronic bronchitis, and lung and nasal sinus cancers. Some sensitised people react when they consume food or water containing nickel or breathe dust containing it.
Selenium	Selenium is a trace mineral needed in small amounts for good health; but, exposure to much higher levels can result in neurological effects, brittle hair and deformed nails.
Silver	Exposure to high levels of silver for a long period of time may result in a condition called argyria: a blue-gray discoloration of the skin and other body tissues.
Thallium	Exposure to thallium occurs mainly from eating contaminated food. Thallium exposure is associated with temporary hair loss, as well as nervous and reproductive system damage.

Table 6. Characteristics of hazardous elements

The EP is specifically designed to simulate the leaching that the waste will undergo from repetitive precipitation of acid rain on an improperly designed sanitary landfill. Repetitive leaching is carried out a minimum of nine times, with separate analyses conducted on each of the resultant leachates. EP is not applicable for the assessment of volatile analytes.

3.2.2 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The TCLP was also developed by the US-EPA as a supplement to the EP toxicity testing method for identification and classification of hazardous wastes. Compared to the EP, the TCLP waste classification is based on a much more extensive list of organic and inorganic compounds and covers a broader range of waste types [4].

The TCLP (TCLP-USEPA Method 1311) is frequently applied to coal combustion products. The buffering solutions (pH 4.93 and 2.88) used in the TCLP were specially designed to simulate landfill conditions [5]. Buffer #1 (pH 4.93) is used for neutral to acidic materials, while buffer #2 (pH 2.88) is used for alkaline wastes. The TCLP uses a 20:1 liquid-to-solid (L/S) ratio (by mass), and the mixture is continuously rotated to ensure mixing for 18±2 hr at 30 rpm.

The US-EPA now recognises that the TCLP is an inappropriate test for use with CCPs [6]. The rather conservative approach of using a more acidic buffer for alkaline materials was designed to accommodate the acidic conditions typical associated with putrescible waste landfills. However, selection of the TCLP for any application other than co-disposal with uncharacterised waste or with putrescible material may lead to incorrect conclusions concerning potential leaching characteristics [7].

3.2.3 SYNTHETIC GROUNDWATER LEACHING PROCEDURE—LONG-TERM LEACHING

The Synthetic Groundwater Leaching Procedure—Long-Term Leaching (SGLP—LTL) procedure was developed at the Energy and Environment Research Centre (EERC) at the University of North Dakota [6]. It was designed to use a synthetic groundwater or distilled deionised water for the leaching solution, to more closely simulate environmental conditions, and to include longer-term leaching time frames for reactive CCPs.

The test was originally designed to simulate leaching under acid rain conditions. The procedure selects an appropriate buffer on the basis of site location with reference to the Mississippi River. For Australian purposes, the test procedure has been modified to include a selection process similar to that of the TCLP (based on waste pH) [5].

The following three buffers may be used:

- pH 4.2 – A 60/40 w/w mix of sulphuric and nitric acid in an appropriate amount of reagent water
- pH 5.0 – A 60/40 w/w mix of sulphuric and nitric acid in an appropriate amount of reagent water
- Reagent water – used for all acid volatile and naturally volatile target analytes.

The complete SGLP—LTL usually includes leaching times of 18 hrs, 30 days and 60 days. However, LTL (30 or 60 days) is only necessary for alkaline samples (pH >10), because CCP samples with pH values below 10 do not undergo long-term hydration reactions that affect leachate characteristics.

It is noted [6] that when distilled, deionised water is used as the leaching solution in the 18-hour SGLP leaching test, that test is equivalent to the ASTM D3987 Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM, 2004). The SGLP with distilled, deionised water uses the same 18-hour time frame, 20:1 L/S ratio, and end-over-end agitation at approximately 30 rpm.

3.2.4 AUSTRALIAN STANDARD LEACHING PROCEDURE METHOD (AS 4439–1997) BOTTLE LEACHING PROCEDURE

ASLP is Standards Australia's version of the TCLP. The main differences between the ASLP and the TCLP are [5]:

- maximum sample particle size (2.4 mm for ASLP and 9.5 mm for TCLP)
- in addition to the standard TCLP buffer solutions, AS4439 allows to use of three alternative buffers depending on the application
- reagent water – applicable when a waste is undisturbed and left on site
- tetraborate pH 9.2 – for acid volatile target analytes and in situation of co-disposal
- local water – when exposure to local ground, surface or seawater is expected.

The buffer solution options available allow ‘waste type’ and ‘disposal situation’ to be included in the decision process.

The ASLP was developed with allowances for variable waste types, including non-putrescible and putrescible waste material. The ASLP has been adopted in Western Australia, South Australia and Victoria. The New South Wales EPA refers to Australian Standards in leachates preparation (AS 4439–1997), but it specifies use of standard solutions of either pH 4.93 ± 0.05 if the pH of the waste sample is less than pH 5.0, or pH 2.88 ± 0.05 if the pH of the waste sample is greater than 5.0. This exactly reproduces the TCLP requirements. In some instances, the New South Wales EPA may permit the use of leachants with a pH different from those specified above. The EPA’s authorisation for using an alternative must be sought in writing and will only be provided with justification for the proposed variation.

As discussed in the previous section, most Australian states use ASLP leaching tests for classification of waste and waste management schemes. A list of trace elements and TCLP/ASLP limits for each state is given in Appendix A.

3.2.5 AMERICAN SOCIETY FOR TESTING AND MATERIALS D3987 STANDARD TEST METHOD FOR SHAKE EXTRACTION OF SOLID WASTE WITH WATER

The ASTM extraction procedure is based on extended extraction with distilled water. This procedure provides a halfway point between acidic TCLP conditions and in-situ conditions, by allowing a leach in deionised water. The ASTM procedure clearly states that the intention is *not* to replicate field conditions, but rather to provide a laboratory benchmark against which various waste types may be assessed [5]. It is designed for rapid production of a leachate from solid waste and estimates the mobility of inorganic constituents. The leach is intended to replicate the soluble portion of a waste when the major contributor to the pH regime is the waste itself. The analytical measurements obtained from ASTM extracts are expected to be more indicative for wider range of field conditions than the more aggressive EP and TCLP methods [4, 8–10].

3.2.6 DIN 38414 S4 SHAKE TEST (EUROPE)

DIN 38414 S4 (DIN-NORMEN, 1984) is a standard batch leaching test, which has been widely used for regulatory compliance purposes in Germany and Austria, as well as for general assessment elsewhere. It uses distilled and deionised water at an L/S ratio of 10:1 for 24 hours, which allows the test material to establish the pH. This test will be superseded for regulatory use by the EN 12457 batch leaching tests and other tests recently developed under CEN TC/292 [11] (see below).

3.2.7 BS EN 12457 (EUROPE)

The minimum leaching requirement for testing for waste acceptance is the European compliance leaching test BS EN 12457. Three-part tests are conducted on waste prepared such that 95% of the sample passes through a 4-mm sieve. The three parts differ only in the L/S ratios at which the test is conducted and the number of leaching steps:

- BS EN 12457 Part 1: single-stage batch tests at L/S ratio 2 L/kg with particle size below 4 mm. Single-step leaching for 24 hours
- BS EN 12457 Part 2: single-stage batch tests at L/S ratio 10 L/kg with particle size below 4 mm. Single-step leaching for 24 hours
- BS EN 12457 Part 3: two-stage batch tests at L/S ratio of 2 L/kg and 8 L/kg with a high solid content and with a particle size below 4 mm. Two-step leaching for 18 hours; the results are aggregated to provide cumulative L/S10 leaching information [12].

The test is used as a characterisation and compliance batch test for granular wastes. The test assesses leachability under mild extraction conditions for waste disposal or material reuse options. The pH of the elute is not externally controlled during this test; i.e., the elute pH is determined by the pH of the waste material itself ('own pH' or 'natural pH'). If it is used as a compliance test, it must also be undertaken as part of a basic characterisation procedure.

As a compliance test:

L/S10 values from the two-step test (Part 3) are required for assessing compliance with waste acceptance criteria leaching limit values at L/S10 for: As, Ba, Cd, Cr, Cu, Hg, Ni, Mo, Pb, Sb, Se, Zn, Cl, F and SO₄, phenol index, total dissolved solids (TDS) and dissolved organic carbon (DOC) in mg kg⁻¹ dry residue. Elute pH should always be determined.

This test is mandatory for assessing compliance with the waste acceptance criteria for inert, hazardous landfill and stable, non-reactive hazardous landfill.

As a characterisation test:

Increasing the L/S ratio represents increased flushing of the waste with water, correlating with leaching timescales. The two-step test provides basic information about relative timescales for release, particularly when compared with maximum availability for leaching and when placed in the context of data from the upflow percolation test.

Testing samples targeted for worst-case as well as average operational conditions, or over different time frames, will highlight whether the waste quality is vulnerable to waste acceptance criteria non-compliance at certain times. Results of the testing may lead to the need to identify alternate management options for the waste or for on-site procedures to be modified.

3.2.8 CSIRO LEACHING TEST PROCEDURE

The CSIRO leach procedure follows that described by Ward *et al.* [13] and is based on earlier CCSD research described by Jankowski *et al.* [14, 15]. This procedure was developed for benchmarking Australian coal ashes and slags and to provide comparative data for comparison with hydrogeochemical modelling results.

In brief, the samples of residues (ashes or slags) are leached for 72 hours in distilled water at L/S ratios of 3.5:1 and 20:1. The leachates are filtered through 0.22-µm Millipore cellulose acetate membrane filters. An unacidified portion of the filtrates is analysed for pH and conductivity. Another portion of the filtrate is acidified to approximately 1% v/v using AR grade concentrated nitric acid and the concentrations of trace elements determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

When an L/S ratio of 20:1 and leaching time of 18 hrs is used, the procedure is similar to the ASTM D3987 method.

3.2.9 COMPARABLE CHARACTERISTICS OF THE LEACHING TESTS

In the United States, the three tests described above are all applied for CCP use. The TCLP is required by most states; but, some states use the Synthetic Precipitation Leaching procedure (SPLP) or the ASTM Standard Shake Test [16]. The states also differ in the standards they use to evaluate leaching tests and to classify the by-products. Typically, the leaching test data are compared with either RCRA standards for characteristic hazardous wastes or an end-use water quality standard. For example, the State of Illinois uses Class I groundwater standards as its leaching test limits and applies the ASTM standard shake test for by-products characterisation.

Regulations in Wisconsin also require the ASTM D 3987 method to be conducted on fly ash before it can be used for stabilising highway subgrades. For an industrial by-product to be acceptable in particular application (e.g. asphalt pavement), aqueous concentrations of five species (Cd, Cr, Se, Ag, and SO₄, because concentrations of these species generally affect the suitability of fly ash for stabilisation) must not exceed 'Category-4' standards stipulated in the *Wisconsin Administrative Code* [17]. This approach has limitations in terms of the ground water impacts: no evidence has been provided indicating that concentrations obtained from the leaching test are the same as those of the leachate discharged from stabilized soil in situ. Another limitation is that the tests are conducted on bulk fly ash samples, rather than on a mixture, and the ash:soil ratio also differs in the field.

Currently, the US-EPA is implementing new characterisation leaching tests in SW-846 to provide more appropriate alternatives for cases in which the TCLP is not scientifically appropriate. The tests include a pH-dependent leaching test, a percolation test, a tank leach test and a compacted granular leach test. They were implemented by formal release of draft methods, followed by inter-laboratory validation. In Japan, China and Australia, these methods are increasingly being recognised as powerful tools to assess potential environmental impact [18].

Comments and comparison of the leaching procedures described above were also given by Ward *et al.* [19]. They suggest that TCLP testing tends to indicate a higher level of leachability for many elements – especially from solids that generate an alkaline leachate solution – than other leaching procedures. This reflects the contrast in pH conditions under which the test is conducted. The EP and TCLP tests are focused on alkaline by-products at conditions that are quite different from those derived from immersion in water alone. Therefore, a similar level of mobility might not be actually obtained from ashes and slags under more natural exposure conditions. This is why the ASLP, ASTM and DIN procedures seem to be more suitable for characterising coal ashes and slags.

Comparison of test conditions of standard leaching procedures used for regulatory purposes is given in Table 7.

Even with exact duplication of regulatory or standard methods, there is only a 60–80% probability that tests conducted by different laboratories with the same protocol will produce statistically comparable results [2]. However, compliance tests and standard methods are not necessarily appropriate for simulation of leaching in the natural environment, obtaining data on reaction mechanisms, or unravelling complex solubility relationships. For these cases, it is necessary to develop a procedure that addresses the experimental objectives, meets the procedural constraints, and produces data that is functionally related to the problem being studied.

To position Australian gasification slags within the range of other coal use products, ASTM (or similar standard leaching tests) should be used to compare trace elements and slag leachability characteristics with other CCPs. For classification of slags from Australian coals and selection of proper waste management strategies, ASLP or TCLP should be used to address characteristics in terms of existing regulations for use and disposal.

Criteria	Method	Test condition	Relevance
Liquid/solid ratio	EP	20:1	Adequate
	TCLP	20:1	Adequate
	ASLP	20:1	Adequate
	ASTM D3987	4:1, 20:1	Overestimated
	DIN 38414	10:1	Overestimated
Extraction liquid	EP	0.5N acetic acid	Aggressive
	TCLP	Acetic acid	Aggressive
	ASLP	Acetic acid, reagent water	Aggressive/adequate
	ASTM D3987	Distilled water	Adequate
	DIN 38414	Distilled water	Adequate
Extraction time, h	EP	24	Underestimated
	TCLP	18	Underestimated
	ASLP	18	Underestimated
	ASTM D3987	18, 48	Underestimated
	DIN 38414	24	Underestimated
pH control	EP	5	Aggressive
	TCLP	2.88 or 4.93	Aggressive
	ASLP	2,88 or 4.93 or none	Adequate
	ASTM D3987	None	Adequate
	DIN 38414	None	Adequate
Agitation condition	EP	Tumbler	Aggressive
	TCLP	Tumbler	Aggressive
	ASLP	Tumbler	Aggressive
	ASTM D3987	Tumbler	Aggressive
	DIN 38414	Tumbler	Aggressive
Temperature, °C	EP	20–40	Adequate
	TCLP	19–25	Adequate
	ASLP	19–25	Adequate
	ASTM D3987	19–25	Adequate
	DIN 38414	19–25	Adequate
Number of extraction	EP	1	Underestimated
	TCLP	1	Underestimated
	ASLP	1	Underestimated
	ASTM D3987	1	Underestimated
	DIN 38414	1	Underestimated

Table 7: Comparison of test conditions of standard leaching procedures

3.3 Chemical and leaching characteristics of coal combustion by-products

3.3.1 COAL COMBUSTION BY-PRODUCTS

The chemical characteristics of CCPs depend on the type and source of coal, the combustion technology, and the pollution control technology employed. From an Australian perspective, coal combustion by-products are almost exclusively sourced from pf combustion plants. This section gives some general characteristics of pf combustion by-products for comparison with those expected from entrained flow coal gasification. It also provides some information regarding the by-products obtained from pressurised fluidised bed combustion of coal (PFBC).

Characteristics of pf fly ashes

Benchmarking of the composition of Australian and international coal ashes was given by Riley [20]. The concentrations of trace elements in coal fly ashes from Australian and international coals were compared, and a summary is given in Table 8.

Trace element	Australia	Europe	North America
As	5–44	22–162	8–304
B	7–89	24–534	130–1660
Be	4–24	3–34	4–17
Cd	0.25–1.34	1–6	0.7–11.7
Co	5.6–100	20–112	6–43
Cr	18–130	47–281	15–229
Cu	28–151	39–254	34–131
Hg	0.02–0.23	<0.01–1.4	0.01–0.22
Mn	88–1630	250–750	237–1307
Mo	5–21	5–22	7–103
Ni	11–242	49–377	13–799
Pb	48–81	40–1075	31–84
Sb	1–4	1–120	2–17
Se	1–5	3–30	2–25
Sn	5–11	4–15	<2–13
V	49–274	154–514	49–3120
Zn	67–283	70–924	49–479

Table 8: Concentration (mg/kg) ranges of trace elements in coal fly ashes [20]

While the range of results is very broad, concentrations of trace elements in Australian fly ashes fall within the ranges found for European and North American fly ashes. Only manganese concentrations vary over a relatively wider range.

Leaching characteristics of international and Australian fly ashes were previously compared using the CSIRO Leaching Test (Section 3.2.8) [20]. These characteristics are compared with TCLP characteristics of 34 North American fly ashes and the corresponding regulatory limits applied in the United States [21]. The results are presented in Table 9.

Trace element	CSIRO			TCLP, North America	Limits*
	Australia	Europe	North America		
As	0.04–2.2	0.01–12	0.02–5	<0.0003–11	5
B	0.4–16.9	1.5–152	34–440	0.2–270	–
Ba	–	–	–	0.05–670	100
Be	<0.003–0.29	0.001–0.14	0.05–0.11	–	–
Cd	<0.003–0.11	<0.001–0.16	0.02–0.58	<0.0001–0.32	1
Co	<0.005–0.11	0.004–0.119	0.02–2.29	<0.0003–0.5	–
Cr	<0.005–0.9	0.02–9.26	0.03–5.2	<0.0003–7.3	5
Cu	<0.006–5.5	0.04–0.34	0.03–0.45	–	–
Hg	–	–	–	<0.0001–0.0005	0.2
Mn	<0.003–7.3	<0.1	<0.002–5.2	–	–
Mo	0.11–5.5	0.35–6.6	0.4–60	–	–
Ni	0.02–3.85	0.03–0.51	0.32–5.8	–	–
Pb	<0.001–0.038	0.006–0.046	<0.001	<0.0002–0.035	5
Sb	<0.001–0.18	0.01–0.618	0.05–0.59	<0.0003–11	–
Se	0.11–1.2	0.05–3.66	0.2–5.41	0.0057–29	1
Sn	<0.001–0.005	0.005–0.013	<0.002	–	–
Tl	–	–	–	<0.0003–0.79	–
V	0.11–8.0	0.05–4.06	0.16–6.8	–	–
Zn	0.03–38.0	0.03–0.72	0.01–5.4	–	–

Table 9: Leaching characteristics of Australian and international fly ashes (mg/l). ‘–’ is unavailable data. *Resource Conservation and Recovery Act limits

All of these fly ash leachates have selenium concentrations that exceed the RCRA limits. Arsenic and chromium are also elements of concern for European and North American ashes. Leaching of barium

is observed for North American ashes, but no such data are available for Australian and European fly ashes.

Characteristics of pressurised fluidised bed combustion of coal by-products

The major differences between ashes from PFBC and those from conventional pf fired power stations are high levels of calcium, barium and strontium in PFBC ashes. The high calcium levels are due to the use of limestone for desulphurisation.

A summary of the characteristics of by-products from PFBC is given elsewhere [22]. The characteristics and behaviour of the by-products from the Tidd PFBC demonstration plant have been widely published [23, 24]. Characteristics of PFBC by-products are presented in Table 10.

By-product leaching data were obtained using both the US-EPA and ASTM methods. The US-EPA test produced higher leachate values of many elements exceeding the drinking water limits. The ASTM leaching test resulted in high values only for cadmium. However, the by-product was not considered to be hazardous based on RCRA limits.

Trace element	TE concentrations, mg/kg		US-EPA, mg/l		ASTM, mg/l		Primary drinking water standards	RCRA limits
	PFBC, bed ash	PFBC Fly ash	PFBC, bed ash	PFBC Fly ash	PFBC, bed ash	PFBC Fly ash		
As	137–139	237–257	0.008	<0.005	<0.01	<0.005	0.05	5
Ba	–	–	2.1	0.78	0.58	0.66	1.0	100
Cd	6.7–7.4	11.0–13.0	0.1	0.04	0.02	0.012	0.01	1
Cr	–	–	0.1	<0.08	<0.08	0.08	0.05	5
Pb	2.8–4.6	33.0–41.0	0.22	0.056	0.03	0.038	0.05	5
Hg	6.6–8.4	8.0–9.4	<0.0002	<0.0002	0.0002	<0.0002	0.0002	0.2
Se	–	–	<0.01	<0.01	<0.01	<0.01	0.01	1
Ag	–	–	0.1	0.06	0.04	0.04	0.05	5
Co	18–20	33.0–36.0	–	–	–	–	–	–
Cu	438–696	621–777	–	–	–	–	–	–
Ni	51–53	75.0–86.0	–	–	–	–	–	–
V	66–84	122–135	–	–	–	–	–	–

Table 10: Trace elements and leaching characteristics for PFBC by-products. Shaded areas indicate if the concentration exceeds drinking water (grey) or RCRA (blue) limits. ‘–’ is unavailable data

Leaching characteristics of pilot-scale and commercially-generated PFBC by-products are shown in Table 11. The table also shows information on atmospheric pressure fluidised-bed combustion (AFBC) systems for comparison.

Trace element	AFBC	PFBS-pilot	PFBC-commercial
As	<0.5	13–30	20–31
Cl	6–381	5-170	4-1580
F	<1	<0.1–3.2	0.6–4.9
SO ₃	–	1–21	3–578
Cd	–	0.4–1.5	0.4–1.6
Cr	–	26–79	20–49
Cu	–	3–27	25–69
Hg	–	<0.5–0.8	<0.5–2
Ni	–	12–34	13–62
Pb	–	7–25	6–15
Zn	<0.3–0.77	<0.3	<0.005

Table 11: Summary of leaching characterisation data for PFBC by-products, mg/l

3.4 Gasification by-products

The characteristics of gasification by-products depend strongly on feedstock properties and the specific gasification technology. This section considers three types of gasification system based on fixed bed, fluidised bed and entrained flow gasifiers. Particular emphasis will be on entrained flow gasifiers, as they have been selected for nearly all the coal-based IGCC pilot-scale and commercial plants currently in operation or under construction.

3.4.1 FIXED-BED GASIFICATION

Solid by-products in fixed bed gasification may appear as dry ash, if the temperature at the bottom of the bed is kept below the ash fusion point (e.g. Lurgi dry-ash gasifier); or as slag, if the temperature at the bottom is sufficient for the ash to melt (e.g. British-Gas Lurgi [BGL] gasifier).

The characteristics of trace elements in the commercial-scale Sasol fixed-bed, dry-bottom (FBDB) gasifiers have been extensively studied in terms of trace element volatility when operating on low rank bituminous South African coal [25–27] as well as on North Dakota lignite [28]. Their concentrations in ashes as a function of bed depth were specified and summary of these investigations is presented in Table 12.

Volatile		Semi-volatile		Non-volatile	
Hg	0.01–0.3	Cu	12.6–47.4	Ba	148–3000
As	2.43–40.74*	Mo	0.2–7.8	Co	2.2–8.8
Se	0.71–1.88	Ni	14.3–198.4	Cr	47–379
Cd	0.10**–0.86	Zn	8.1–42.1	Mn	85–319
Pb	0.94–19.1			V	27.9–106.3

Table 12: Concentration of trace elements (mg/kg) in Sasol ash bed. *High values are for North Dakota lignite. **Low values are for North Dakota lignite

The distribution of trace elements was found to change as a function of ash bed depth. The results for the volatile trace elements for North Dakota coal ashes were, in general, similar to those for the South African coal ashes. North Dakota ashes have only higher concentrations of arsenic and lower concentration of cadmium when compared with the South African gasifier ‘ashes’. Both the slag (or ash) discharge in the BGL and the Lurgi gasifiers and the oxygen injection tuyeres are at the bottom of the gasifier; hence, full reducing conditions may not be achieved in the slag/ash formation zones of these systems. This may affect the composition of the slag/ash when compared with most entrained flow gasifier systems where the slag leaves the gasifier in a more reducing zone (often through the same outlet as the syngas).

Leaching characteristics of these ashes were also studied [29]. The water leaching test (DIN38414-T4) and TCLP leaching test were conducted in three analytical laboratories, and the results were compared to the South African department of Water Affairs and Forestry (DWAF) standards and TCLP regulatory levels. The results of the tests are presented in Table 13.

In the water leaching test (DIN 38414-T4), the pH values for all leachates from the gasification plant were high (10.9–12.6) due to the presence of OH⁻ ions produced from the hydrolysis of CaO. It was noted that TDS in the gasification ashes were six times lower than those in conventional power station ashes from South African coals [29].

The TCLP leaching test used acidic leaching as a worst case scenario to assess the mobility of trace metals. Despite some variation in the leaching results from different laboratories, none of the leachates generated from the gasification ashes exceeded both ES EPA TCLP and the DWAF regulatory limits. Therefore, the ashes were not classified as hazardous waste materials.

Trace element	DIN 38414-T4	TCLP	TCLP limits	DWAF limits
As	<0.0043	0.001–0.026	5	0.43
Ba	–	0.393–1.17	100	7.8
Be	–	–	–	–
Cd	<0.0025	0.001–0.02	1	0.031
Co	<0.001	–	–	–
Cr	0.004–0.006	0.01–0.99	5	4.7
Cu	<0.0011	–	–	–
Pb	<0.023	0.002–0.013	5	0.1
Hg	–	0.001–0.014	0.2	–
Se	–	0.003–0.073	1	0.26
Ag	–	0.001–0.025	5	2
Al	6–13	–	–	–
Fe	0.012–0.019	–	–	–
Mn	<0.00034	–	–	–
Mo	<0.0070	–	–	–
Ni	<0.0061	–	–	–
V	0.017–0.020	–	–	–
Zn	0.128–0.139	–	–	–

Table 13. Leachate analyses results for Sasol gasification fly ashes. ‘–’ is unavailable data

3.4.2 FLUIDISED BED GASIFICATION BY-PRODUCTS

The temperature in fluidised bed gasifiers is kept below the ash fusion temperature, to avoid clinker formation and possible de-fluidisation of the bed. Commercial fluidised bed gasifiers differ in ash conditions (dry or agglomerated) and in design configurations for improving char use. There are relatively few large fluidised bed gasifiers in operation.

Samples generated in the fluidised bed gasifier at the DOE’s Power Systems Development Facility (PSDF) in Wilsonville, AL (now called the National Carbon Capture Center) were investigated for their trace elements concentrations and their leaching characteristics were assessed using a column leaching test [30].

Samples generated in the fluidised bed gasifiers were highly alkaline. While the leachate pH was high in all cases, the cations tended to be more soluble in the acidic leachants.

Characteristics of PSDF residues are listed in Table 14.

Trace element	% leached	Concentration in leachate, mg/l	MCL, mg/l	RCRA limits, mg/l
Sn	–	0.01–0.0012	0.006	–
As	8.56–15.0	0.007–0.009	0.01	5
Ba	29.9–34.4	15.49–20.52	2	100
Be	0.41–0.71	<0.001	0.004	–
Cd	1.21–4.0	<0.001–0.001	0.005	1
Cr	0.59–1.2	0.001	0.1	5
Cu	0.03–0.08	0.004–0.019	1.3	–
Pb	0.06–0.37	0.005–0.006	0.015	5
Hg	–	<0.002	0.002	0.2
Se	12.25–36.0	0.016–0.041	0.05	1
Al	1.17–4.78	88.9–102.2	0.05	–
Fe	1.26–3.02	0.088–0.119	0.3	–
Mn	11.25–14.83	<0.001–0.001	0.005	–
Zn	0.17–0.59	0.008–0.01	5	–

Table 14: Characteristics of PSDF residues. Shaded data exceeds corresponding shaded colour limit. ‘–’ is unavailable data

While the solubility of arsenic, antimony, and selenium were low for the PSDF samples, they were highest in the high pH leachant, which is typical of oxyanions [30]. Concentrations of tin, barium, aluminium and iron exceed United States primary or secondary drinking water standards (maximum contaminant level, MCL), but are well below the RCRA limits, so these by-products are not classified as hazardous materials.

3.4.3 ENTRAINED FLOW GASIFICATION BY-PRODUCTS

IGCC by-products include coarse and fine slag, fly ash and spent sorbent from the gas cleaning process, elemental sulphur (a commercial grade by-product), and, in some cases, combinations of these streams. The specific by-product streams vary based on the particular IGCC process technology and the properties of the feedstock used. IGCC slag is generally the highest volume by-product, and based on available literature, is the most characterised in terms of chemical and physical properties and their impacts on disposal and use options [22].

Slag

IGCC slags have bulk chemical properties similar to some coal combustion by-products, specifically boiler slag and bottom ash (see Table 15). These products are often used in engineering or manufacturing applications, suggesting that IGCC by-products may be managed (at least in part) through use rather than disposal.

Table 16 compares trace element contents of typical IGCC slags with those of boiler slag and bottom ash [22, 31]. The chemical composition of IGCC slags varies widely, and numerous trace constituents are present at very low levels. This reflects the variability of the composition of the coal and other process inputs, which can complicate predictions of waste properties based on averages.

A summary of the IGCC by-product leaching characteristics is given in Table 17 [22]. Most of these characterisations are based on by-products from the Tampa and Wabash River IGCC plants.

	IGCC slag	pf boiler slag	pf bottom ash
SiO ₂	10–64.9	40.5–53.6	45.9–70.0
Al ₂ O ₃	3–29.6	13.8–22.7	15.9–28.3
Fe ₂ O ₃	0.1–25.7	10.1–14.3	2.0–14.3
CaO	2.7–49	1.4–22.4	0.4–15.3
MgO	0.7–7	5.2–5.6	1.9–5.2
Na ₂ O	0.3–4	0.7–1.7	0.6–1.0
K ₂ O	<0.1–4.6	0.1–1.1	0.1–1.3

Table 15: Comparison of properties of IGCC slag, boiler slag, and bottom ash (wt.%) [22]

Trace element	PC boiler slag	Gasification slag*
Sb	0.25–1.0	4.8–< 10
As	0.01–254.0	6.39–< 10
Ba	6.19–1720	37.9–80
Be	7.0–7.0	2.03–10.9
B	0.1–55.0	128–283
Cd	0.01–40.5	0.76– <50
Cr	1.43–5981	29.6–120
Cu	1.37–156	12–54.1
Pb	0.40–120.0	8.19–97
Hg	0.016–9.5	0.03– < 0.08
Ni	3.3–177	22.9–146.7
Se	0.010–14.0	3.02– < 10.0
Ag	0.01–74.0	< 1.0–3.0
Tl	33.5–40.0	< 0.4–16
V	75.0–320.0	25.1–156
Zn	4.43–530	32.97–213

Table 16: Trace elements (mg/kg) of IGCC Slag with slag from PCC plants [31]

Gasifier	BGL	PRENFLO	GSP			Texaco			
Coal	Pittsb. #8	Pittsb #8	Walsam Rohfein Kohle	East Ellbian Brown	West Ellbian Brown	SUFCo	Illinois #6	Pittsb. #8	Lemington
Test	EPA-EP	EPA-EP	DIN	DIN	DIN	EPA-EP	EPA-EP	EPA-EP	EPA-EP
Ag	0.001	0.001	<0.001	-	-	<0.002	<0.002	<0.002	<0.002
As	0.003	0.001	<0.001	-	-	-	<0.002	<0.002	0.003
B	1.070	0.21	<0.1	-	-	-	-	-	-
Ba	0.402	0.03	0.085	<0.001	<0.001	0.32	0.086	0.086	0.096
Be	-	0.001	<0.001	-	-	-	-	-	-
Cd	0.002	0.001	<0.001	-	-	<0.002	0.013	0.003	0.008
Co	0.025	0.041	0.0031	<0.001	<0.001	-	-	-	-
Cr	0.053	0.0014	0.0013	<0.001	<0.001	<0.005	<0.005	0.006	<0.009
Cu	0.83	0.0037	0.0015	<0.001	<0.001	-	-	-	-
Hg	ND	0.001	<0.001	-	-	<0.001	<0.001	<0.001	<0.001
Mn	2.06	0.028	0.0019	<0.001	<0.001	-	-	-	-
Mo	0.003	0.001	0.0026	-	-	-	-	-	-
Ni	0.075	0.19	0.033	<0.001	<0.001	-	-	-	-
Pb	0.007	0.001	<0.001	-	-	0.08	<0.002	<0.001	0.004
Sb	0.011	0.001	<0.001	-	-	-	-	-	-
Se	-	0.001	<0.001	-	-	<0.08	<0.03	<0.003	<0.003
Sn	-	0.001	<0.001	-	-	-	-	-	-
Tl	-	0.01	<0.001	-	-	-	-	-	-
V	-	0.001	<0.001	-	-	-	-	-	-
Zn	0.11	0.021	<0.01	-	-	-	-	-	-

Table 17: Leaching characteristics of IGCC slags, mg/l. ‘-’ is unavailable data

Characteristics of slag fractions

Raw gasification slags generally consist of vitrified coarse fraction (Frit) and carbonaceous fine fractions (CFF). These slag fractions from the Wabash River Power plant [32] were characterised from a materials development point of view [11]. The characterisation included both ASTM and TCLP leach tests (see Table 18).

The results were compared with Illinois water quality standards (from Illinois regulations perspective) and with EPA TCLP limits (from other states’ perspective).

	ASTM		TCLP		Illinois water quality standard		EPA TCLP hazardous waste limits
	FRIT	CFF	FRIT	CFF	Class I	Class II	
pH	4.37	7.06	4.84	4.87	6.5–8	6.5–8	
mg/kg							
As	0.02	0.08	0.07	0.08	0.05	0.2	100
B	2.96	0.11	0.14	3.38	2	2	1
Ba	0.16	0.16	0.63	0.25	2	2	1
Cd	0.24	0	0	0.21	0.005	0.05	5
Co	0.39	0	0.11	0.34	1	1	5
Cr	0.002	0	0	0.02	0.1	1	5
Cu	0.32	0	0.25	0.28	0.65	0.65	5
Fe	0	0.01	10.03	0.2	5	5	5
Pb	0	0	0.07	0.2	0.0075	0.1	20
Mn	0.08	0	0	0.11	0.15	10	5
Ni	37.41	1.68	13.04	35.06	0.1	2	5
Ag	0	0	0	0	0.05	0.05	20
Se	0.2	0	0	0.35	0.05	0.05	20
Zn	14.4	0.01	0.39	14.25	5	10	20

Table 18: Leaching characteristics of FRIT, ASTM test [11]. Shaded data exceeds corresponding shaded colour limit

Table 18 shows that the FRIT fraction yielded leachates that were acidic. The CFF fraction yielded leachates that were neutral. In both the by-products, the pH and almost all of the trace material concentrations were more or less consistent over a period of 18 hours.

Both the FRIT and CFF yielded highly acidic leachates at the end of the standard TCLP test. For the characteristic metals tested – arsenic, barium, cadmium, chromium, lead, selenium and silver – the leachate concentrations were below the regulated TCLP limits for both the FRIT and CFF fractions.

However, in the case of the FRIT, boron, cadmium, nickel, zinc, selenium and iron exceeded both the Illinois Class I and II water quality standards. Arsenic exceeded the Class I standard, but not the Class II. In case of CFF, cadmium, lead, nickel, selenium and zinc exceeded both the Class I and II standards. Arsenic exceeded the Class I but not the Class II limit.

Characteristics of IGCC by-products from blended feedstocks

Trace elements in the samples of residues generated in the Polk IGCC plant and Puertollano have been determined [30, 33]. Concentrations of trace elements in by-products, including slags, fly ashes (for Puertollano) and fine high-carbon particulates (for Polk) are listed in Table 19.

	Polk		Puertollano		IGCC range
	Fine particulates	Slag	Fly ash	Slag	Slag
Sb	–	–	412–544	<0.01–4.5	4.8 – < 10
As	69–161	–	613–707	7.0–9.3	6.39 – < 10
Ba	327–1197	542–806	386–440	574–647	37.9 – 80
Be	9–42	5–29	9–14	7.3–10.9	2.03–10.9
B	ND	ND	453–519	51–66	128–283
Cd	10–12	<0.01–1.0	17–22	<0.01–0.4	0.76– <50
Cr	169–525	552–629	123–195	99–123	29.6–120
Cu	121–383	103–119	269–353	28–56	12–54.1
Pb	73–182	0–125	2855–4063	5–8	8.19–97
Hg	0.026–0.1	–	0.0003–0.0048	0.0012–0.0022	0.03– < 0.08
Mn	207–496	429–482	ND	ND	ND
Ni	2687–11,223	2720–4073	1031–2153	342–828	22.9–146.7
Se	67–161	–	4–11	0.3–8.0	3.02– < 10.0
Ag	ND	ND	–	–	< 1.0–3.0
Tl	ND	ND	13–19	<0.01–7.4	< 0.4–16
V	ND	ND	2813–5591	1681–3444	25.1–156
Zn	341–1649	17–140	5785–7788	13–25	32.97–213

Table 19. Trace elements (mg/kg) in IGCC by-product from coal-petcoke blends. ‘–’ is below the detection limit. ND, not determined

The use of petroleum coke with high V and Ni contents significantly increases the amount of Ni and V in by-products, including slag samples, compared with the average range of IGCC slags trace element concentrations for gasification of coal alone.

In fly ashes and fine high-carbon particulates, a high concentration of lead, zinc and copper is also observed. While the amount of fine particulates produced in slagging gasification units is significantly less than in pf combustion systems, the concentrations of Zn, Pb, As, Sb, Cd, Cu, V, Ni, and Mo in fly ash are around one order of magnitude higher than the concentrations of PCC fly ashes [33]. The high enrichment of IGCC fly ash in the above elements is likely associated with high slag/fly ash ratio of the entrained flow gasifiers compared with pulverised coal combustion (90:10), which accounts for the high content of condensing material with respect to the non-volatile components. Of course, for similar coals, in absolute values the total amount of metals and semi-metals present in gasification and combustion by-products are similar, or even lower in IGCC with coal-petcoke feed.

Relatively high contents of Pb, Sb, Zn in the Puertollano ashes is directly linked with high content of these elements in the Puertollano coal.

Leaching behaviour of by-products obtained from gasification of coal with other feedstock has also been studied [30, 34]. Six samples (two slags and four high-carbon particulates) were obtained from a commercial gasifier using coal and pet coke [35].

Column leaching tests were used to simulate the reaction of granular materials during exposure to fluids such as landfill leachate, acid rain, or acid mine drainage. Two of the six samples generated in a commercial IGCC unit had relatively little effect on leachate pH. The neutral and acid leachants generated acidic leachates from the other four samples. The maximum leachate concentrations of Fe, Ni and Zn were very high for the acidic IGCC samples generated from a mixture of coal and petroleum coke. The maximum concentration of these elements, particularly Ni, was much higher than from the alkaline samples or from typical PC fly ashes.

The cations Al, As, Be, Co, Cr, Cu, Fe, Mn, Ni, and Pb were slightly or moderately soluble in the acidic residues. The ions Sb and Zn were moderately or very soluble. For the alkaline IGCC samples, Al, As, Co, Fe, Mn, Ni, and Pb were slightly soluble; Ba, Ca, K, Mg, Na, and Se were slightly or moderately soluble. The Hg concentration was relatively low.

The results of the leaching test for certain elements are presented in Table 20 and compared with standard limits.

	% leached		Concentration in leachate, mg/l		MCL, mg/l	RCRA limits, mg/l
	Fine particulates	Slags	Fine particulates	Slags		
Sn			0.001–0.007	0.002–0.0135	0.006	
As			0.006–0.047	0.004–0.019	0.01	5
Ba	0.23–6	0.1201.3	0.054–0.574	0.220–0.274	2	100
Be	4.33–14	4.9–11	0.002–0.226	0.001	0.004	
Cd	0.7–11	0.01–0.4	0.889–2.947	0.001	0.005	1
Cr	4.9–36	3.3–4.7	0.012–0.073	0–0.002	0.1	5
Cu	8.8–44	8.3–18	0.007–25.182	0.008–0.046	1.3	
Pb	0.14–14	7.5	0.006–0.089	0.002–0.087	0.015	5
Hg	–	–	–	–	0.002	0.2
Se			0.109–1.429	0.022–0.099	0.05	1
Al	3.4–1.5	0.6–3.2	1.82–949.2	0.067–1.046	0.05	
Fe	3.3–37	5.1–7.3	0.016–1.88	0.023–1.767	0.3	
Mn	8.3–35	2.8–2.9	3.285–25.96	0.005–0.22	0.005	

Table 20: Leaching characteristics of IGCC solids from gasification of coal-petcoke blends [27]. Shaded data exceeds corresponding shaded colour limit. ‘–’ is unavailable data

Except for Hg, most of the cations in a few leachate samples were at high concentrations, which often exceeded primary or secondary drinking water standards by a factor of 10–1000. This could be a constraint in any use in which the IGCC residue was exposed to an aqueous solvent.

However, note that the:

- leaching procedure used in this work was a column leaching test that was used as a comparative test
- leachant solutions had wide range of pH (1.2–11.1) and were aggressive for some of the residues.

Characteristics of leachates from Puertollano IGCC plant by-products are available for selected elements only [36]. Leaching tests for germanium (Ge) shows high extraction yields using pure water due to the unusual occurrence of soluble GeO_2 . High leaching of Ni is also observed, which exceeds the limits applied for by-products disposal. Nickel is mainly present in sulfides, and an oxidizing media is needed in order to obtain acceptable extraction yields. Vanadium is mainly associated with the aluminium-silicate matrix, and an alkaline extractant is required for the selective extraction. Therefore, these residues require additional treatment before their disposal.

Gasification residues resulting from the use of delayed oil sands coke, Genesee sub-bituminous coal, Boundary Dam lignite, and blends were also obtained in the CANMET pilot-scale gasifier [34]. Samples of slag collected after the runs were analysed for their leaching potential using the TCLP procedure. The concentrations of the controlled elements were well within the Alberta Environment's associated limits listed for the leachates.

Results presented in this section indicate that gasification slags are generally non-leaching or low-leaching materials for most of the standard leaching tests applied. Some of the slags obtained from coal-petcoke blends gasification, however, have relatively high leachability and could be an issue for disposal options.

3.4.4 IGCC BY-PRODUCTS FROM AUSTRALIAN COALS

While Australian coals have been used extensively in some of the IGCC demonstration and commercial projects internationally, there are only limited data regarding trace element concentrations and behaviour in slags and other by-products. While samples of slag and other solid by-products are typically difficult to obtain, some recent work undertaken as part of the CCSD test of Australian coals in a Siemens pilot-scale gasifier, provided an opportunity to produce samples of slags and other process solids under realistic conditions. As part of that work, the samples were characterised in terms of their concentrations of trace elements, and some preliminary measurements of their leachability were made.

In related CCSD work [37], some samples of slag from an Australian coal (S256) gasified in the Buggenum IGCC (Shell) gasifier were also obtained, and characterised in terms of their trace element concentrations and leachability.

This section presents an overview of the relevant outcomes of these activities.

Details regarding the testing of Australian coals in the Siemens pilot-scale gasifier can be found in [38, 39]. These tests produced a slag product, which was quenched and removed through a slag hopper, and a second stream of finer solid particles, which were removed from the gas and washed out with the quench water. These finer particle samples removed from the process water stream have been labelled 'process water solids', and consist of fly slag, fly ash, and unconverted carbon.

These samples were analysed using a number of chemical and microstructural techniques, including chemical analysis for bulk composition and trace elements, X-ray diffraction (XRD), and leaching

behaviour (using the procedure developed by CSIRO)[40-42]. These slags and fly ashes were also characterised from a regulatory perspective using ASLP and TCLP test procedures.

The coal samples and their gasification residues are listed in Table 21. Slag discharged through the slag tap is the major mineral matter product for all of the tests. The amount of process water solids (fine slag particles and unburnt carbon) is quite high for coal 701 (34%), but the solid residues produced from gasification of the other three coals contained a lower proportion (5–18%) of fine particles, which were carried from the gasifier in the process water stream. However, fine slag from the coal 703 test contains a significant amount of apparently unmelted solids, including solid CaO (as result of fluxing this coal with limestone CaCO₃).

In the slag tapped from the quench unit, Coals 702 and 703 had a higher proportion of fine slag particles (<1 mm) than Coals 701 and 704. No fine particles (<1 mm) were found in the tapped slag produced from Coal 704 and the entire sample reports as coarse quenched particles. This coal also produced a relatively small proportion of process water solids. This result indicates that, under the conditions used in these tests, the coal mineral matter was almost fully melted to produce a coarse glassy slag product.

Coal/slag	CRC701/T100	CRC701/T101	CRC702/T102	CRC703/T103	CRC704/T104
Frit (>1 mm)	61.5	70.5	34.5	9.0	92.0
Fine slag (<1 mm)	4.3	4.6	59.8	72.7	0.0
Fly ash	34.1	24.6	5.5	17.8	8.0

Table 21: Fractions (%) of solid by-products from gasification of Australian coals in Siemens pilot gasification facility

Samples of by-products characterised for their trace element concentration and leaching characteristic are listed in Table 22. These include raw slag (as tapped) and process water solids. The slag component identified as 'Frit' is the portion of the tapped slag that reports as clearly defined glassy droplets. Other tapped slag components recovered from the slag lock hopper include fine slag particles and larger glassy particles, which are often broken as a result of rapid quenching. In commercial systems, the larger slag lumps are often crushed as part of the slag discharge system.

Coal	CRC701	CRC702	CRC703	CRC704	S256
Slags	T100, T101	T102	T103	T104	T105
Frit (>1 mm)	s100, s101	s102	s103	S104	
Fly ash	a100,101	a102	a103	a104	

Table 22: Australian coal gasification by-product samples characterised for trace elements and leaching

Characteristics of slags

Compositions of raw slags are shown in Table 23 and Table 24. Some of the raw slag samples contain unreacted carbon (particularly s102 and s103) and some unprocessed (not molten) minerals (particularly s100, s102, s103). Slag compositions for major elements are typical for coal gasification residues.

Trace element concentrations in the slags from these Australian coals are generally in the range of those reported elsewhere [43] for gasification slags produced from similar coals. There are some clear coal-specific variations regarding the presence of barium, chromium, copper, mercury, nickel, thorium, and vanadium.

The coarse slags fraction (Table 24) has one order of magnitude less arsenic, boron, fluorine, mercury, lead, tin, antimony and zinc than the raw slags. These elements are classified as volatile and highly volatile; however, as discussed later, they can be recaptured by fly ash. Therefore, their higher concentrations in raw slag indicate the presence of fly ash and/or unprocessed solids in the discharged slag samples. For comparison, trace element concentrations in the frit fraction are shown in Table 25.

Test	T100	T101	T102	T103	T104	T105
Moisture	0.3	<0.1	0.6	0.6	<0.1	<0.1
Ash yield	99.8	100.4	89.5	71.3	100.0	99.8
C	1.1	1.7	11.7	21.6	0.9	1.4
Amorphous phase	85.5	97.9	86.1	74.6	100.0	100.0
Al ₂ O ₃	21.5	18.9	21.2	21.5	32.1	22.0
CaO	9.94	4.86	7.21	12.8	7.31	14.9
Fe ₂ O ₃	21.5	23.2	13.2	3.16	5.84	6.73
K ₂ O	0.48	0.45	0.22	0.47	0.60	0.78
MgO	2.80	2.18	0.77	0.93	2.08	1.12
Mn ₃ O ₄	0.12	0.09	0.08	0.03	0.03	0.05
Na ₂ O	1.51	0.58	0.06	0.72	0.96	0.22
P ₂ O ₅	0.64	0.85	1.52	1.21	0.14	0.16
SiO ₂	41.5	48.2	41.6	34.8	51.1	54.5
SO ₃	0.60	0.45	0.43	0.32	0.05	0.22
TiO ₂	0.85	1.13	1.33	1.03	1.68	1.07

Table 23: Bulk chemical composition of slags, wt.%

Trace element	T100	T101	T102	T103	T104	T105	Gasification slags
As	9.3	1.4	4.8	2.2	0.8	2.7	6–10
B	200	64	160	40	91	120	128–283
Ba	2900	3600	2200	480	1300	840	38–80
Be	9	17	5	3	6	9	2–11
Bi	0.79	nd	nd	nd	nd	nd	–
Cd	0.2	nd	0.18	0.16	nd	nd	<0.76
Cl	300	40	65	68	nd	73	–
Co	61	100	41	56	38	51	–
Cr	1000	780	200	190	200	93	30–120
Cu	100	71	91	53	56	29	12–54
F	200	90	220	380	90	60	–
Hg	0.09	0.02	0.23	0.3	nd	nd	<0.08
Li	64	29	35	150	67	62	–
Mn	890	660	590	150	260	390	–
Mo	200	27	14	6	14	4	–
Nb	35	47	17	10	15	16	–
Ni	240	240	320	98	79	76	23–147
Pb	35	8	12	17	4	nd	8–97
Sb	1.9	0.4	0.5	0.6	nd	0.2	5–<10
Sc	15	18	25	18	32	26	–
Se	1.7	0.5	0.9	0.9	0.2	nd	<10
Sn	34	12	38	27	8	nd	–
Sr	2400	2200	1400	390	1400	530	–
Th	28	40	15	13	17	17	<0.4–16
U	9	11	4	5	6	6	–
V	150	140	110	87	240	170	25–156
W	17	13	5	4	4	5	–
Y	82	120	67	44	63	73	–
Zn	180	75	62	130	17	10	33–213

Table 24: Concentrations of trace elements in slag samples, mg/kg. Shaded data exceeds values reported elsewhere for typical gasification slags. nd, not detected; ‘–’ is unavailable data

Trace element	s100	s101	s102	s103	s104	Range
As	0	0	0	0.2	0.1	0.1–0.2
B	11.6	1.2	1.4	1.7	nd	1.2–11.6
Ba	3800	4600	3000	790	1200	790–4600
Be	14	18	8	4	3	3.0–14
Cd	0.9	0.6	0.47	0.40	0.29	0.29–0.9
Co	76	101	52	69	75	52–101
Cr	707	197	392	202	108	108–707
Cu	48	52	85	55	62	48–85
F	80	nd	40	80	70	<80
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Li	36	20	46	182	226	20–226
Mn	620	610	690	240	180	180–620
Mo	18	19	10	5	3	3–19
Ni	188	244	328	120	86	86–328
Pb	2.1	1.5	1.6	0.9	0.6	0.6–2.1
Sb	0.19	0.03	0.09	0.04	0.05	0.03–0.019
Sc	46	45	52	45	41	41–52
Se	0.34	0.34	0.76	0.13	0.08	0.08–0.76
Sn	0.9	0.6	1.0	0.3	0.4	0.3–1.0
Sr	2300	2400	1900	670	450	450–2400
Th	35	42	21	15	14	14–42
U	8.2	9.7	5.3	5.0	4.8	4.8–9.7
V	240	123	134	120	104	104–240
W	4.4	3.6	2.5	2.1	2.1	2.1–4.4
Y	83	99	69	47	41	41–99
Zn	32	19	17	20	19	17–32

Table 25: Trace elements in coarse slag (FRIT), mg/kg. nd, not detected

Characteristics of Fly Ash

As noted above, most of the coal mineral matter is removed from the gasifier through the slag hopper as a dense slag phase. A relatively small proportion of the coal mineral matter reports as fine particles and can be carried from the quench vessel in the recirculating quench water stream. Most

of the fine solid material removed from the gasifier in the circulating process water is classified as fly ash, with some fly slag. The differentiation in these two classifications reflects the fact that the latter (fly-slag) particles have been formed from small molten droplets of slag. Compositions of these materials collected from the pilot plant tests are listed in Table 26 and Table 27.

These data are compared with the compositional range of a range of (unrelated) combustion and gasification fly ashes previously reported [20, 41]. Most of the trace element concentrations (except possibly selenium, tin, strontium and zinc) for the gasification fly slags and ashes from these Australian coals lie within the broad experience range reported for trace element concentrations for other gasification slags produced in a variety of gasifiers from a fairly broad range of coals.

Pilot scale fly ashes					
	a100	a101	a102	a103	a104
SiO ₂	35.4	35.1	45.8	49	49.33
Al ₂ O ₃	26.2	24.9	23.5	23.3	23.9
Fe ₂ O ₃	23.5	24	12.4	3.7	7.17
CaO	3.35	3.4	5.63	12.6	7.4
MgO	2.4	2.3	0.53	0.93	2.33
P ₂ O ₅	2.45	2.67	5.4	2.53	0.33
Na ₂ O	0.9	0.77	0.37	1.17	1.6
K ₂ O	0.45	0.47	0.47	1.17	0.77
SO ₃	1.7	1.8	2.1	1.3	1.93
TiO ₂	1.35	1.27	1.57	1.03	1.9

Table 26: Major elements in gasification-derived fly ash and fly slag, wt.%

Trace element	100	101	102	103	104	Range	Fly ash [20]
As	16	27	105	2	28	2–105	5–162
B	71	51	219	37	86	37–219	7–534
Ba	5900	6500	3700	500	1900	500–6500	NA
Be	31	35	9	3	9	3.0–35	3.0–34
Cd	5.1	5.9	4.4	1.2	1.7	1.2–5.9	0.4–6.0
Co	112	157	47	68	228	47–68	6.0–100
Cr	138	139	136	48	63	48–139	15–281
Cu	161	316	323	121	152	121–323	34–254
F	650	580	3700	1900	700	580–3700	N/A
Hg	1.32	1.8	10.7	1.77	1.36	1.32–10.7	N/A
Li	27	24	52	229	70	24–229	N/A
Mn	960	960	600	140	260	140–960	88–1630
Mo	70	65	19	8	20	8.0–70	5–103
Ni	241	281	516	123	159	123–516	11–799
Pb	210	221	173	106	247	106–247	31–1075
Sb	3.9	2.9	3.2	4.2	3.9	2.9–4.2	1–120
Sc	34	37	54	47	77	34–77	N/A
Se	7.5	13.1	92.1	6.3	2.7	2.7–92.1	1.0–30
Sn	27.0	22.0	16.0	12.0	21.0	12.0–27.0	5.0–13.0
Sr	3400	3500	2200	560	2100	560–3500	49–3120
Th	42	44	18	22	31	18–44	N/A
U	11.2	13.0	5.5	7.8	8.4	5.5–13.0	N/A
V	144	148	166	141	300	141–300	N/A
W	8.6	8.8	2.6	2.4	4.8	2.4–8.8	N/A
Y	120	127	68	53	95	53–127	N/A
Zn	1374	1440	300	1115	386	300–1440	49–924

Table 27: Concentrations of trace elements in pilot gasifier fly ashes. Blue shaded data exceeds values typically reported for fly ashes

Partitioning of Components between Process Streams

An important outcome of the pilot gasification test program was the identification of partitioning of species between the different process streams (i.e. fly ash and slag in the process water stream, fine

and coarse slag particles in the slag discharge hopper, and condensed volatile species in gas product stream). Trace element species partitioning between the various process streams can be categorised according to their melting and flow behaviour and their volatility:

1. Low volatile, partially lost from slag and fly ash
 - known from the literature to be low or partially volatile
 - some have escaped in gas phase or water
 - some amount remains in fly ash and slag.
2. Volatile, recaptured on fly ash
 - known from the literature to be volatile
 - present in PWS but at higher concentration than in the parent coal mineral matter.
3. Highly volatile from slag and/or fly ash
 - lost to gas or water process streams
 - low concentrations in PWS and/or slag.

These categories can be further subdivided as per Table 28.

Group	Appearance	Experimental		Modelling	
		Slag	Fly ash	Slag	Fly ash
1.1	Low volatile, some loss in slag/fly ash	Th, Sc, Y, Li, Mn, Ni, Sr, Ba		?	?
1.2	Low volatile: recaptured on fly ash		→ Cu, W, Mo, Cd	Y	N
1.3	Low volatile: concentrated in slag	Cr, V	←	N	Y
2	Volatile, recaptured on fly ash		→ Bi, Zn, Sn, Sb	Y	N
3.1	Highly volatile: depleted in slags only	As, Se		Y	?
3.2	Highly volatile: significant loss from solid phases	B, Hg, F, Pb		Y	N
4	Questionable: coal-specific	Nb, U Co, Be		?	?

Table 28: Distribution of trace elements in slag and fly ash. ‘Y’ indicates that the behaviour is consistent with thermodynamic modelling; ‘N’ indicates that the behaviour is inconsistent with thermodynamic modelling; ‘?’ not clear. Arrows indicate how trace elements are re-distributed

Slag leachability: CSIRO test

To study the effect of leachate media on total leachability of the elements, slag leaching experiments for the raw slags were conducted at two L/S ratios (3.5 and 20).

An L/S ratio of 20:1 is used for ASTM standard procedure and was selected as the benchmark to compare leachability of raw slag with FRIT. It is assumed that the FRIT fraction is similar to the slags after beneficiation procedures and could have different uses (to be discussed later).

Preliminary study of the leachability of the Siemens trial slags indicated that variation in the morphology (i.e. particle size and shape) may affect the leaching characteristics of a particular slag. Hence, in the present study, leachability tests were conducted for 'as received' slags and for crushed slag samples (particle size is ~1 mm), since the slag is likely to be crushed for different uses. The range of element concentrations in leachates for each set are shown in Table 29.

Generally, the overall leachability (or solubility) of elements from the slags is low and is below acceptable limits [42]. Comparison of leachate concentrations from different slag fractions and leached at different conditions indicates that:

- total extraction of Al, Fe, P, Si, As, Cd, Co, Cr, Cu, Se, V, W and Zn depends on leachate amount. It does not decrease proportionally in leachates with high L/S ratio, which means that the leaching potential still remains for these elements
- leachability of most elements in the slags containing CFF fraction is higher
- leachability increased with slag crushing for most of the major elements and for some trace elements: As, B, Li, Th, U, W, Y.

In an earlier CCSD report, Riley [20] quoted results for trace elements in leachates (L/S ratios of 20:1) from fly ashes from conventional pf-fired power stations in Australia. In Table 30, the ranges are listed and compared with the observed concentration ranges of a number of trace elements for the ashes or slags (from the transitional technologies) studied in this work [37]. Some of the trace elements in the gasifier slags do not leach as readily as those in the fly ash from conventional power stations; these trace elements are B, Cr, Mn, V and Zn and possibly Co and Cu. However, there does not appear to be any differences in the leachability of the other trace elements, including As and Se. Certainly, IGCC slag has a larger particle size and is less soluble than ash.

The leachability of major slag elements, such as Mg, Na, K, S, and P, is very low; the amount of each element in the leachates is generally less than 0.001 % of the total amount in the slag.

The trace elements can be grouped into categories, depending on their leachability:

4. *High leaching elements* are the elements whose amount in the leachate is ~1% or more of the amount in the slag (in bold, Table 2). These elements are Mo, W, B, As, Zn, Se, and Sb. However, the last five correspond to trace elements which are generally vaporised from the slag, so only Mo and W are likely to be of concern.
5. Elements with *moderate leaching* properties, where the amount of element in the leachate is 0.01–0.5% of the amount in the slag. These elements are Ni, Co, Li, Sc, and Cd.
6. Elements with *low leaching* properties (<0.01% of amount in the slag), such as Sr, Ba, Mn, Y, Th, and U.
7. Element with *leachability not detected* (and not shown in the table) are Cu, Cr, Sn, Bi, Hg, F, and Pb. Within this list, only Cu and Cr are conserved in the slag; all others are in the slag at very low concentrations.

Coal-specific issues influence the leaching results presented above:

- There is relatively high leaching of Zn from slags from CRC701 and CRC702 coals.
- Antimony is leached from slags from CRC702 and CRC704.
- There is relatively high leaching of As, Se, and Mo from CRC703 and CRC704 slags.
- The same elements with moderate leaching or low leaching were observed for almost all four slag samples.

	Raw, L/S=3.5:1	Raw, L/S=20:1	Frit, L/S=20:1	Frit crushed, L/S=20:1	Limit*
pH	7.82–9.09	7.72–9.83	7.61–8.47	8.11–9.49	
Condy*	0.08–0.79	0.02–0.24	0.7–2.3	1.4–9.6	
mg/L					
Al	0.126–5.864**	0.162–3.843	0.005–0.13	0.07–2.03	
Ca	8–142	1.9–9.6	0.2–1.49	0.53–4.3	
Fe	0.02–0.15	0.02–0.42	0.015–0.048	0.009–0.044	
K	0.3–1.86	0.25–0.7	0.1–0.6	0.1–0.3	
Mg	0.58–4.65	0.12–0.89	0.05–0.1	0.18–0.81	
Na	4.53–9.19	1.21–3.38	0.06–0.15	0.13–0.63	
P	1–0.77	0–0.68	0.02–0.06	0.03–0.22	
SO4	18–255	0.9–85	0.36–1.47	0.9–6.6	
Si	0.18–1.59	0.18–1.16	0.11–0.26	0.7–2.06	
µg/L					
As	1.06–8.9	0.71–24.8	0–0.2	0.2–1.1	50
B	10–140	<10	1.2–2.2	2.7–4.5	1000
Ba	4–350	2.1–171	2.0–14	0.9–8	1000
Cd	2.75–3.14	2.67–2.99	0–0.05	<0.01–0.04	5
Co	0.41–2.08	0.2–1.37	2.0–3.0	0–2.0	
Cr	0.8–1.75	0.53–0.71	<0.03	<0.3	50
Cu	0.81–2.42	0.92–1.85	0–2.0	0–2.0	
Li	9.0–85	1.24–9.51	0.3–1.5	2.1–15.2	
Mn	0.39–240	0.1–17	0.9–18	0.9–4	
Mo	19–239	6.0–37.82	1.0–8.8	1.1–13.4	
Ni	1.0–21	0.46–11.47	6.0–35	4.9–13	100
Pb	0.12–1.42	0.15–0.65	<0.2	<0.2	50
Sb	1.39–10.3	0.2–4.17	0.03–0.07	0.04–0.3	
Sc	–	–	<0.2	0.3–0.7	
Se	6.0–57	1.2–37	0–0.26	<0.01–0.26	10
Sr	74–2074	16–594	7.0–21	12.0–30	
Th	0–0.08	0–0.2	0–0.005	<0.004–0.011	
U	0.11–0.75	0–0.07	<0.01	<0.01–0.02	
V	0–7.49	0–8.43	<5	<5	
W	0.64–8.45	0.23–2.95	<0.1	0.4–0.7	
Y	–	–	0–0.018	0.011–0.054	
Zn	2.9–9.2	4.0–12.0	4.0–14	<5	

Table 29: Concentrations of elements in leachates and leachate characteristics. *Water quality guidelines for recreational purposes: general chemicals [44]. *Shaded: in Column 2, leachability increased with leachate amount; in Column 4, leachability is affected by CFF; in Column 5, leachability increased with crushing

Leachates (20:1) of ash or slags from conventional and transitional technologies				
	Convention pf	FBC	Oxy-fuel	IGCC
pH	4.4–12.0	8.6–12.3	6.3–7.7	7.3–9.8
mg/L				
As	<2–20	0.3–2.1	7–60	0.2–25
B	60–945	<200–800	460–7280	<10–40
Be	<0.2–16	–	–	–
Cd	<0.2–5.5	0.05–0.13	0.4–1.1	2.8–3.0
Co	<0.2–145	0.6–1.2	0.6–21	0.2–1.4
Cr	<1–48	1.8–37	1.3–13	0.5–0.7
Cu	<1–275	0.2–1.4	1–9.3	0.9–1.9
Mn	<0.2–365	<0.2–2118	37–795	0.1–24
Mo	5–275	22–52	92–224	1.5–50
Ni	1–193	0.4–3	5–99	0.5–12
Pb	<0.2–1.9	<0.2–8	<0.2–0.2	<0.2–0.7
Sb	<0.1–9	<0.1–2	2.0–6.0	0.2–4.2
Se	3–60	1–37	12–72	1–37
V	5.6–70	<5–125	56–285	<5–9
Zn	< 1–1900	8–11	10–290	3–12

Table 30: Comparison of leachates from ash/slag from conventional and transitional technologies (data extracted from Riley (2007)). ‘–’ is unavailable data

The data presented here are specific to only a small selection of coals and their slags, and are not sufficient to support a general assessment of coal properties and their impacts on trace element partitioning and leaching from gasification residues. However, such information is important, and will form the basis of ongoing work in this area.

The deportment of trace elements in fly ash is different than in slags. Therefore, the leaching of some of the trace elements from gasification-derived fly ash samples could be considerably different to that from the slags. To confidently manage the handling, disposal, or use of solids from entrained flow gasification, ongoing work in this area is required.

Table 31 summarises trace element concentrations and leachability for these Australian coal gasification by-products. Only Cr, Cu and V (highlighted) in the slags and Se, Zn (highlighted) in fly ash may give rise to some concerns in terms of their concentrations in the by-product, and potential leachability.

Concentrations						
	High, slags	High, fly ash	Average slags	Average, fly ash	Low, slags	Low, fly ash
High leaching, leachate volume-dependent		Se, Zn	Mo, W	Mo, W, As, Sb	B, As, Zn, Se, Sb	B
Low leaching, but leachate volume-dependent	Cr, Cu, V		Al, Fe, P, Si, Cd, Co	Al, Fe, P, Si, Cd, Co, Cr, Cu, V		
High leaching, but leachate volume-independent						
Low leaching and volume-independent	Ba, Ni, Th	Sr, Zn				

Table 31: Elements of concern in Australian coal gasification by-products. Shaded are the elements of potential concern

ASLP/TCLP leaching tests are required to characterise and classify slags and fly ashes from Australian coals in terms of Australian waste regulations.

Application of the regulatory ‘coal ash exemption’ (Australian context) on gasification by-products from Australian coals

Earlier sections discussed relevant regulations related to coal use products, including recent coal ash exemption criteria. Using data reported in Tables 24, 25 and 27, the available samples of solid gasification by-products from Australian coals are assessed in terms their compliance to the ‘Ash exemption criteria’.

Table 32 indicates that, on the basis of their bulk composition, none of the by-products (all fly ashes, coarse slags and frit slags), would be automatically exempted. This is mainly because the concentrations of nickel, chromium (except a103 fly ash) and copper (except Buggenum slag) are well above the maximum concentrations listed in the ‘Coal ash exemption’ criteria (see Table 3).

Chemicals and other attributes	Absolute maximum concentration*	Fly ash	Coarse slag	FRIT slag
Mercury	1	All	All	All
Cadmium	1	None	All	All
Lead	50	None	All	All
Arsenic	20	a100,103	All	All
Boron	150	All except a102	All except t100,102	All
Chromium (total)	50	a103	None	None
Copper	40	None	T105	None
Molybdenum	20	a100,103	All except T100,102	All
Nickel	50	None	None	None
Selenium	20	All except a102	All	All
Zinc	70	None	T102, 104, 105	All
pH range	6–13	All		

Table 32: List of gasification by-products that meet ‘Coal ash exemption’ criteria (absolute maximum concentration)

Table 32 also indicates the differences in compliance of the different by-products to requirements of particular elements. Frit fractions of the slags do not exceed limits for all elements except those mentioned above, while ash samples comply only for mercury concentrations.

Classification of gasification fly ashes and slags from Australian coals in Australian regulations

Based on trace element concentrations, slags and fly ashes produced from gasification of Australian coals can be positioned in some Australian states waste classification schemes. As mentioned in Section 2, New South Wales, Australian Capital Territory, and Western Australia regulations in the first stage of waste assess the total concentration (TC) of each trace element and leaching tests are not required for waste classification if the element concentration does not exceed the limit. It is appeared that all analysed by-products from gasification of Australian coal have at least one element of which the concentration exceeds these limits. Details of the elements exceeding the limits in particular state regulations are given in Table 33.

By-product	New South Wales	Australian Capital Territory	Western Australia
Raw slag			
T100	Cr, Ni, Mo	Cr, Ni	Al, Cr
T101	Cr, Ni	Cr, Ni	Al
T102	Ni	Cr, Ni	Al
T103	Ni	Cr, Ni	Al
T104	Ni	Cr, Ni	Al
T105	Ni	Cr, Ni	Al
Frit			
s100	Ni	Ni	Al
s101	Ni	Ni	Al
s102	Ni	Ni	Al
s103	Ni	Ni	Al
s104	Ni	Ni	Al
Fly ash			
a100	Pb, Ni	Pb, Ni	Al
a101	Pb, Ni	Pb, Ni	Al
a102	As, F, Pb, Hg, Ni, Se	As, F, Pb, Hg, Ni, Se	Al
a103	Pb, Ni	Pb, Ni	Al
a104	Pb, Ni	Pb, Ni	Al

Table 33: Elements of slags and fly ashes from gasification of Australian coals that exceed lowest limits in Australian state regulations

Therefore, for all by-products characterised in this section, ASLP and TCLP tests are required to complete their classification in current Australian regulations. Leaching tests described in this section are used for indicative purposes and as comparable tests for different fractions of by-products, and cannot be applied for regulatory purposes.

3.5 Characteristics of steelmaking slags

Discussion of the characteristics of steelmaking slags is relevant, due to their widespread use. Steelmaking slags are usually classified into the following categories [45]:

Air-cooled blast furnace slag (BFS) is a by-product of iron manufacturing, in which silica and alumina constituents combine with lime to form a molten slag collected on the top of the iron in a blast furnace. The slag issues from the furnace as a molten stream at 1400–1600 °C. If this is allowed to cool slowly, it solidifies to a grey, crystalline, stone-like material known as air-cooled slag. This product is then crushed and screened to sizes suitable as coarse aggregate.

Granulated blast furnace slag or slag sand is the product of rapid quenching of molten blast furnace slag with an excess amount of water to produce a sand-like product. In Australia, granulated slag is used primarily in the production of ground granulated blast furnace cement. Excess amounts of such granulates can be used as a fine aggregate (coarse sand). The chemical composition of slag sand is similar to that of air-cooled blast furnace slag. Because of the rapid quenching process, however, its structure is more amorphous.

Electric arc furnace slag (EAF) is a by-product of steel formed in an electric arc furnace. In the process, steel scrap and fluxes are added to a refractory lined cup-shaped vessel. This vessel has a lid through which carbon electrodes are passed. An arc is induced between the scrap and electrodes, and the resultant heat generated melts scrap and fluxes. Steel and slag are also separated similarly to the steel furnace slag process.

EAF slag contains different forms of iron oxides, and most also include magnesium and manganese compounds. The major hydrate compounds in EAF slag are quick lime (CaO), magnesium compounds and calcium silicates, with amounts present depending on the source of the slag.

Steel furnace slag is a by-product of steel formed in the Basic Oxygen System (BOS). BOS slag is tapped from the vessel after the exothermic refinement of molten iron and recycled steel in the presence of fluxes and oxygen. It consists of calcium silicates and ferrites combined with fused oxides of iron, aluminium, calcium, magnesium and manganese. After air-cooling, the material has a predominantly crystalline structure and is crushed and screened for use as coarse aggregate.

Typical slag compositions are shown in Table 34.

	Air-cooled BFS [45]	Granulated BFS [46, 48]	EAFS [47]	BOS [45]
CaO	41	30.9–46.1	30–35	35
SiO ₂	35	30.5–40.8	10–12	14
Fe ₂ O ₃	0.7	0.12–4.72	22–29	29
MgO	6.5	1.66–17.31	5–8	7.7
Mn ₃ O ₄	0.45	0.07–3.12	4–7	5.7
Al ₂ O ₃	14	5.9–17.6	4.5–5.5	5.5
TiO ₂	1.0	0.07–3.7	0.5–1.0	0.5
K ₂ O	0.3	0.08–1.51	0.1–0.3	0.1
Cr ₂ O ₃	<0.005	<0.005	1–2	1
V ₂ O ₅	<0.05	<0.05	0.5–1.0	0.3
S	0.6	0.6–0.8	0.1–0.3	0.1

Table 34: Steelmaking slag compositions, wt%

The principal constituents of iron and steel slags are silica (SiO₂), alumina (Al₂O₃), calcium oxide (CaO), iron oxides (FeO_x) and magnesia (MgO), which make up 95% of the composition and are similar to coal slags. The composition of steelmaking slags differs from coal gasification slags in that they generally have higher CaO and lower SiO₂ and Al₂O₃ contents. Minor elements include manganese, iron, and sulfur compounds, as well as trace amounts of several others. The physical characteristics, such as density, porosity, and particle size, are affected by the cooling rates of the slag and its chemical composition.

In terms of the form, blast furnace granulated slag typically occurs as a glassy (amorphous phase) form, which is similar to the tapped coal gasification slags.

Trace elements concentrations and leachability of steelmaking by-products have been assessed in terms of Australian regulations [49]. Characteristics of iron and steel slags were compared against current nominated or required thresholds, where provided, for each jurisdiction. Table 35 shows average values of trace element concentration for four types of steelmaking slags. Total metals, TM, concentrations of air-cooled BSF, granulated BFS, EAFS and BOS samples were determined well below the maximum TM values specified under Table 35 of the Exemption requirements [49]. Concentrations of chromium, copper, nickel and zinc were relatively high, but within acceptable limits in EAFS and BOS. TCLP leaching tests were conducted for these slags.

Trace element	Air-cooled BFS	TM (max)	Granulated BFS	TM (max)	EAFS	TM (max)	BOS	TM (max)
As	0.5	10	0.5	10	1.3	10	0.6	N/A
B	33.3	N/A	46.7	N/A	73.3	N/A	43.3	N/A
Ba	193.3	N/A	316.7	N/A	560.7	N/A	29.2	N/A
Be	6.7	20	7	20	2.5	20	2.5	20
Cd	0.03	1	0.03	1	0.2	1	0.14	1
Co	2.5	N/A	2.5	N/A	2.5	N/A	3.3	N/A
Cr	7.3	100	5.3	100	4047	20000	509	2000
Cu	1	20	2.3	20	94.9	200	14.3	40
Hg	0.05	1	0.1	1	0.05	2	0.05	1
Mn	1273	N/A	1593	N/A	27260	N/A	15617	N/A
Mo	2.5	10	2.5	10	0.037	70	3.5	100
Ni	10.8	20	7.3	20	19.8	100	19.5	60
Pb	2.5	20	2.5	20	3.8	50	2.5	20
Sb	2.5	N/A	2.5	N/A	2.5	N/A	2.5	N/A
Se	0.5	5	0.5	5	0.5	5	0.5	5
Sn	5	N/A	5	N/A	5.7	N/A	5	N/A
Zn	2.5	50	6.3	50	209.2	700	49	100

Table 35 : Trace elements in some example steelmaking slags, mg/kg. N/A, not available

Table 36 demonstrates that for the few samples considered here, only chromium and nickel were above the TCLP maximum values specified in New South Wales regulations.

Trace element	Air-cooled BFS	Granulated BFS	EAFS	BOS	TCLP max
Cr	N/A	N/A	0.337	0.025	0.2
Cu	N/A	N/A	0.027	0.025	0.2
Mo	N/A	N/A	0.037	0.005	0.2
Ni	N/A	N/A	0.147	N/A	0.1
Zn	N/A	N/A	0.575	0.29	1

Table 36: TCLP leachate concentrations from some example steelmaking slags, mg/L. Shaded data exceeds TCLP limit

Long-term leaching tests were reported for EAF and Ladle slags from a Portuguese steel producer[50]. Leaching tests with both these materials were performed, using a column leaching test to simulate the leaching behaviour of steel slags under landfill conditions. The chemical analysis of the leachates during the tests for both types of slag indicates an increase of heavy metal releases with ageing. The standard test method DIN 38414-S4 was used to evaluate leachability of heavy metals by water in unprocessed slags. After more than one year of trials, slag samples submitted to these trials presented very low total leaching levels. The most easily leached elements were calcium and magnesium. Nevertheless, in the column leach test, calcium and magnesium contents leached from solid slags are below 0.5%, and all other metals below 0.1% of the concentrations in the slags. Leachates obtained with DIN 38414-S4 present, as expected, higher leaching values; however, these are less than 5 % (Ca) and 1% (other elements).

To address potential questions regarding the safety of current and future uses of steelmaking slag, the Steel Slag Coalition, United States, initiated a comprehensive study that culminated in the development of risk assessments for EAFS, BOS, and BFS slag types [51]. The study used worst-case exposure assumptions in the risk calculations and several possible exposure scenarios to ensure the general applicability of the risk assessment conclusions.

Slag samples were analysed using EPA analytical methods, including:

- total concentrations of major and trace metal constituents
- TCLP of certain metals
- ASTM tests for certain metals
- bioaccessibility of certain metals
- particle size distribution.

The slag samples were analysed for the following metals: antimony, aluminium, arsenic, barium, beryllium, cadmium, calcium, carbon, chromium (total), chromium (hexavalent), cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, phosphorous, selenium, silicon, silver, sulfur, thallium, tin, vanadium and zinc.

Leachates were analysed to determine if the metals present in the slag could be mobilised by dissolution under both acidic and neutral conditions. Weak acidic conditions, simulated under the TCLP test, are presumed to occur in sanitary, hazardous or industrial waste landfills. The concentration of metals in slag present at levels greater than background were compared with various state, regional EPA, and federal EPA health-based screening criteria for both residential and non-residential (i.e. industrial, construction, commercial) scenarios. If a metal exceeded at least one of these agency criteria, it was retained for analysis in the risk assessment.

In addition, the results of the TCLP and ASTM leaching tests were used to determine if any metals in slag would potentially affect groundwater and surface water bodies. These test results were compared to the appropriate TCLP/drinking water quality standards and EPA Ambient Water Quality Criteria.

The initial screening process allowed the risk assessment to focus on a limited set of slag constituents (chemicals of interest). In general, the levels of metals in steelmaking slag were lower than expected, and, similarly, leachability was found to be very low. Table 37 presents the slag constituents that were identified through this screening process for further evaluation in the risk assessments. The constituents are grouped according to the relevant screening criteria.

Slag type	Residential	Non-residential	Groundwater	Ecological
EAFS	Sn, Cd, Cr (total), Cr (hexavalent), Mn, V	Cr (total), Mn, V	None	Al, Ba
BOS	Cd, Cr (total), Mn, Ta, V	Cr (total), Mn, V	None	None
BFS	Be, Cr (total), Mn	Be, Cr (total)	None	None

Table 37: Metals in steelmaking slags evaluated in the risk assessment and identified as requiring further evaluation [49]

The following risk assessments, however, demonstrated that BF, BOF, and EAF slags are safe for use in a broad variety of applications and pose no significant risks to human health or the environment. The results show that:

- Carcinogenic and non-carcinogenic risks associated with steelmaking slag are insignificant for potentially exposed residential populations, farmers, and industrial users.
- Metals in steelmaking slag will not leach readily to groundwater or surface water in amounts that exceed concentrations in drinking water.
- Steelmaking slag will not significantly affect animals and other terrestrial life in or near areas of application.
- Steelmaking slag may be applied safely (no effect on water quality and aquatic life) in aquatic environments such as rivers, lakes and streams, which normally provide sufficient dilution to protect against possibly elevated pH levels, and in the case of EAF slag, potential concentrations of aluminium and barium.

3.6 Summary

This section has provided an overview of the procedures used to determine the environmental characteristics of slags, and a review of recent data concerning some of the potentially environmentally harmful species that may be found in slags and other by-products from coal gasification. It has given some insight into the important leaching tests that can be used to characterise the potential of such by-products to cause environmental harm. The results of these leaching tests may vary between laboratories, demonstrating the importance of standard, comparative tests such as the ASLP and TCLP tests.

Gasification slags are generally non-leaching or low-leaching materials for most of the standard leaching tests applied (unless the slags are obtained from gasification of coal-petcoke blends). Generally, slags demonstrate lower leachability of trace elements compared with their leachability from fly ashes. This low leachability usually leads slags to be classified as non-hazardous materials. However, some results indicate that leachates from some slags and gasifier fly ashes do have trace element concentrations that may be of environmental concern. Also, in some instances, the total concentration in the bulk by-product may also be of concern.

This review has shown that standardised leaching tests need to be developed that can provide a realistic assessment of the likely environmental behaviour of gasification residues. Although it is frequently stated that gasification slags are environmentally benign, some of the research described above indicates that this may not always be the case, and some of the other gasification products, such as fly ash, may be more reactive than previously realised. More research is required to provide relevant data to properly assess the likely environmental impacts of gasification by-product disposal or use.

Partitioning of trace elements is observed in solid residues from coal gasification. Trace element concentrations differ in fly ashes, raw slags and coarse slags, and affect the leaching characteristics of by-products. Concentrations of trace elements in by-products were evaluated in terms of the compliance of by-products to 'Coal ash exemption' requirements (mainly for land fill application). Frit fractions of the slags have lower concentrations of the hazard specified elements, but as for other by-products (coarse slag and fly ashes), it exceeds limits in concentration of nickel, chromium and copper. Taking into account the lower leachability of the slags than fly ashes from conventional (combustion) fly ashes, this indicates that gasification by-products have to be assessed differently in terms of environmental regulations.

It is also important to consider a more advanced approach by focusing on gasification by-product use options, rather than by-product disposal.

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4 Current practices for use of coal combustion and gasification by-products

This section provides an overview of current practices in disposal and use of coal combustion and gasification by-products. Section 5 describes current practices in the use of slags from the iron and steelmaking industry.

Although gasification is a mature technology in the international chemical industry, its application to power generation is still in the commercial demonstration stage, and only about six commercial coal-based IGCC plants are currently operating. Therefore, the use practices for IGCC by-products are still in the development stage.

Gasification (and hence IGCC) slags have a number of properties similar to vitreous forms of iron slags, and granulated blast furnace and BSF slags. Fly ash is also an IGCC by-product, albeit a minor one; it has similar characteristics to those of pf ash, as shown in Section 3. Therefore, it is most likely that IGCC by-products will find similar applications, and the discussion in this section and the next is based upon this assumption.

4.1 Current practices in ash use

4.1.1 THE AUSTRALIAN EXPERIENCE

In 2010, approximately 14.1 million tons of CCPs were produced in the Australasian region, of which about 5.8 million tons (41%) had been effectively used to some beneficial end. This includes about 1.9 million tons (14%) that were used in high value-added applications such as cementitious applications or concrete manufacture. The remainder (59%) was disposed of either on-site or at nearby facilities in storage dams or in dry disposal. Of the beneficially used ash, the majority (about 24%) was used in projects that typically generate no economic return, but do supply a cost avoidance or recovery; such projects include on-site mine remediation and local haul roads.

The driving forces behind increasing CCP use include:

- minimising disposal costs
- enabling other uses of the land and decreasing disposal permitting requirements
- financial returns from the sale of the by-product, or at least an offset of the processing and disposal costs
- using CCP products to replace some expensive natural resources [1].

The main beneficial applications of fly ash include, but are not limited to [1, 2]:

- Aerated concrete blocks: fly ash forms the primary material within the blocks, which are widely used in house and office buildings.
- Ready-mixed and precast concrete: fly ash that has been classified or selected to appropriate standards is widely used as an addition in concrete, partially replacing Portland cement.
- Grouting of mines and caverns: fly ash is widely used for stabilising large voids in the ground, allowing it to be returned to productive use and remediating problems of subsidence. It compares favourably in this application with naturally occurring aggregates.
- Fill and ground remediation: fly ash has been extensively used for building embankments, restoring old quarries, etc.

- Blended cement and cement raw material: fly ash is increasingly used by cement manufacturers both as a source of silica, and as a blend material. This enables them to produce more environmentally friendly and cost-effective cements, reducing overall CO₂ emissions, energy and use of natural aggregates.
- Roadway and pavement use: hot rolled asphalt is another application where fly ash replaces the limestone dust. Fly ash can be worked at much lower temperatures than conventional material, requires less energy in preparation, and has a lower bulk density and performed well in service [3].
- Infiltration barrier and underground void filling
- Soil amendment
- Environmental improvement (e.g. water treatment).

There is a large body of literature relevant to the use of fly ash for agricultural application. The relevant properties of fly ash include [4]:

- readily available in large quantities
- often has a high pH for neutralisation of acidic soils
- high trace element content
- ability to retain more water than most soils
- loosening effect when mixed with tight and heavily textured soils.

The issue in this arena is application and dosage. Some trace element concentrations are particularly high, and excessive dosages can be dangerous.

Furnace bottom ash is less widely used than fly ash. In part, this due to the fact that bottom ash constitutes a much smaller proportion of total station ash production, and thus incurs a greater relative cost in handling and management in ash use programs. Bottom ash is used mainly in concrete blocks, cement, bricks, tiles, aggregates, road construction, embankments, structural fill and surface mine reclamation. Additional applications include medium/low technology road construction, mainly as a substitute for sand and gravel; blasting grit, concrete and grouting material, aggregates, snow and ice control [5].

4.1.2 CCP USE: THE INTERNATIONAL EXPERIENCE

Table 38 illustrates production and use of fly ash around the world in 2001–03.

North American practice

The United States utility and construction materials industries have nearly doubled the beneficial use of coal ash from 22% in 1989 to 43% in 2007 [6]. Fly ash has been used in the construction of roadways and interstate highways since the early 1950s.

Of the beneficial CCP uses, 39% of fly ash was in the manufacture of concrete products, grout, blended cement structural fills and waste stabilisation; bottom ash principally as a structural fill and flue gas desulphurisation (FGD) in the production of gypsum panel products (7.29 million t). Almost all fluidised bed combustor (FBS) ash was used in mining application (11.43 million t), and almost all boiler slag (1.83 million t) was used as blasting grit and roofing granules (1.62 million t).

The latest available data shown in Table 39 (2009) indicate the production of fly ash and other CCPs in the United States [6]. In 2009, 135.700 million tons of CCPs were produced and 55.64 million tons were used (41%).

Country	Year	Production (kT)	Proportion used (%)
Australia	2002	12500	32
Canada	2002	4744	21
China	2002	150000	66
Denmark	2002	729	98
EU15	2002	43047	89
India	2001–2002	100000	23
Israel	2000	1300	98
Japan	2002	9300	83
Netherlands	2003	996	~100
South Africa	2002	22000	30
UK	2002	5500	55
USA	2002	76500	35

Table 38: International fly ash production and use comparison [4]

By-product	Fly ash	Bottom ash	FGD Gypsum	FGD wet scrubbers	FGD dry scrubbers	FBS ash	Boiler slag	Total
Amount, million t	63.00	16.60	18.00	11.70	10.62	12.53	2.18	135.70
%	46.7	12	13	8.5	7.7	9.1	1.6	100

Table 39: CCP production in the United States (2009)

In Canada, the primary uses of fly ash are in:

- cement manufacturing
- hydraulic mine backfill (cement replacement)
- liquid waste stabilisation
- flowable fill (used for backfill, excavation, sub-base, road base etc.)
- concrete
- mineral filler [8].

European practice

In 2006–08, about 60 million tons of CCP were annually produced, of which fly ash was the major portion (66–68%) [9, 10]. Other CCPs produced include FGD gypsum (11.21 million t, or 18.4%),

bottom ash (6.14 million t, or 10%), boiler slag (1.77 million t, or 2.9%), FBC ash (936 million t, or 1.5%).

As shown in Table 38, much of the CCPs produced in Europe are beneficially used. The principal uses of fly ash are (in million tons):

- cement raw material (5.25)
- blended cement (2.65)
- concrete addition (6.20)
- general engineering fill (1.47)
- structural fill (1.15)[9].

The major application of bottom ash was in the production of non-aerated blocks (1.26 million t from 3.11 million t total used), and the main application of boiler slag was in blasting grit and pavement base course (0.82 million t and 0.62 million t, respectively). More than 50% of the FGD-gypsum used was in plaster board production (5.56 million t).

4.2 IGCC by-products and their use

As already detailed (Section 3), coal mineral matter (mostly as slag) and sulfur are the major solid by-product streams produced by IGCC systems. Most prominent coal gasification processes incorporated into IGCC, such as Shell, GE, E-Gas and Siemens, are slagging systems that operate at high pressure. As for slags produced in combustion systems, gasifier slags may be expected to be suitable for applications such as blasting grit, roofing tiles and other construction building products, and as aggregate for asphalt roads. Sulfur is usually recovered and sold as elemental sulphur or sulphuric acid.

4.2.1 INDUSTRIAL PRODUCTS FROM IGCC SLAGS

Slag-Based Lightweight Aggregate

The pelletising process and the use of pelletised lightweight slag in structural and masonry concrete have been documented for more than 30 years [11]. This process is applicable to a wide range of slags and the products have significant production and usage advantages when compared with conventional expanded vesicular slag.

Slag-based lightweight aggregates are produced by duplicating the processing methods used for commercial lightweight aggregate (LWA) manufacture. It includes grinding the slag, mixing it with a clay binder and water, and extruding it to form long strands that are cut to the desired size. These wet green pellets are then dried and calcined.

Fly ash and slags generated in the ELCOGAS power plant (Puertollano IGCC) have been demonstrated to be suitable for recycling as LWA [12]. No leaching of hazardous elements was detected and microtoxicity of leachates of LWA was found to be harmless. The Electric Power Research Institute (EPRI), and the Illinois Clean Coal Institute have conducted a United States Department of Energy (DOE)-funded project, along with considerable industry involvement. The project has demonstrated the technical and economic feasibility of commercial production and use of slag lightweight aggregates (SLA) and ultra-lightweight aggregates (ULWA) [13]. SLA was found to be an excellent substitute for conventional LWA in roof tile, block and structural concrete production. ULWA material may also be used as a partial substitute for expanded perlite in agricultural and horticultural applications.

Cement Additives

For application of IGCC slags to cement manufacturing, grinding of coarse slag to a very fine particle size is required to evaluate its pozzolanic characteristics. A feasibility study was conducted on the use of a slag/lime mixture as a partial replacement in slag Portland cements [14]. The pozzolanic reactivity of the slag improved, with increasing basicity and CaO content in slag, and decreasing of the degree of condensation of silicate ion in the glass phase. Hydrated products produced from the slag cement were not very different from those from blast furnace slag cement. The compressive strength of the high calcium slag cement (gasified slag B) was almost equal to that of blast furnace slag.

The University of Kentucky has conducted a project investigating the potential use applications of coal gasification by-products [15]. As a part of their study, frit components of slags produced at Polk station and Eastman Chemicals gasifiers were evaluated for their pozzolanic characteristics. Fine-ground slags from both gasifiers showed pozzolanic activity in mortar cube testing and met the ASTM C618 strength requirements after only three days. Pozzolanic activity was also examined using British Standard 196-5. Neither aggregate showed significant potential for undergoing alkali-silica reactions when used as a concrete aggregate, according to ASTM test method 1260.

Sand blasting grit or other abrasive applications

Crushed slags from coal-fired utility boilers and smelter slags are commonly used for abrasive blasting at shipyards. Slags have the advantage of low silica content, but have been documented to release other contaminants, including hazardous air pollutants, into the air [16].

However, the slag needs to be fully characterised as to its suitability. In a recent study of Turkish industrial wastes, coal slags, blast furnace and steelmaking slags were evaluated as blasting abrasives [17]. It was found that only converter slag met all the specifications for abrasives and could be used in blast cleaning operations. However, coal furnace slag, granulated blast furnace slag and ferrochrome slag were found to be unsuitable for use as an abrasive in surface preparation technologies. Although the granulated blast furnace slag from the Ereğli Iron and Steel Works had a good cleaning performance, it could not be used as an abrasive in preparation of steel, since it left local traces of contamination on the worked surface. The coal furnace slag from the Çayırhan thermal power plant did not provide the minimum cleaning performance and created excessive dust, prohibiting its use as an abrasive in blast cleaning operations.

Other IGCC solid residue potential use options

Where conversion levels are low, gasification slags may contain significant quantities of unburnt carbon and these have been used as a supplemental, pulverized coal combustion fuel. The carbon-rich gasification by-products were also evaluated as a precursor of activated carbons at The Pennsylvania State University Energy Institute [18]. The carbons in gasifier chars were thermally treated and chemically activated and then tested for mercury (Hg) adsorption potential. The results from this work indicated that certain gasifier slag carbons have the potential to capture Hg from combustion flue gas. This is unlikely to be a realistic by-product use pathway, as most commercial gasification processes will be tuned to ensure maximum carbon conversion in the gasification unit.

4.2.2 PATENTS ON GASIFICATION BY-PRODUCTS USE

Many patents related to gasification slag use have been lodged in the past 25 years and reflect the efforts on finding gasification slag/fly ash use options. These patents can be grouped in two categories:

- slag beneficiation/treatment

- slag/fly ash industrial application.

Most of these patents address the use of slags and fly ashes in building applications.

The first group includes:

- US 5,647,876 'Method of removing volatile metals from slag using an acid wash' patented by Winter et al, 1997 [19]: applies to the recovery of condensed solidified volatile metals from the slag that exits the reactor section of a partial oxidation reactor
- US 6,706,199 'Method for withdrawing and dewatering slag from a gasification system' patented by Winter et al, 2004 [20]: includes an apparatus and method for withdrawing and dewatering slag from a gasification system that discharges the fully processed slag at the outlet ready for transportation
- US 7,651,563 'Slag crusher' by Gruhlke et al, 2008 [21]
- WO/2009/155666 'Granulation of molten materials' by Xie et al., 2009 [22]: a granulator comprising a rotary atomiser for receiving molten material and projecting droplets of the molten material.

The second group includes patents on slag applications in the cement industry and concrete aggregates:

- US 4,701,222 'Process for producing an artificial light-weight aggregate', Kobayashi et al. 1987 [23]: describes a process of preparation of artificial light weight aggregates with a specific compositional range of SiO₂, Al₂O₃, Fe₂O₃, and at least one oxide selected from the group consisting of MgO and CaO, and specific gravity and crushing strength corresponding to that of fly ashes obtained from a boiler of a coal-fired power plant using Australian coal
- US 4,969,932 'Flyslag treatment utilizing a solids-containing concentrated aqueous stream and a cementitious material', by Potter et al., 1990 [24]: describes a process for the treatment of flyslag from the gasification of coal, which includes mixing of the fly slag with a cementitious material and a residual waste stream from a coal gasification process; the waste stream contains particulate flyslag solids. A composition comprising fly slag and a cementitious material, in specified proportions, is also disclosed
- US 5,073,197 'Cement compositions' by Majumdar et al., 1991 [25]: describes a 50:50 mixing with silica fume, gasifier slag, fly ash or other pozzolanic or latently hydraulic material, which preserves characteristics of high-alumina cement (early strength, resistance to sulphate attack) and eliminates disadvantages such as age weakening
- US 5,166,109, 'Utilization of slag from coal gasification systems' by Alpert et al., 1992 [26]: describes a low-density aggregate product and method for making by using coal ash slag resulting from a typical coal gasification system, the resulting aggregate product having a lower density than the initial coal ash slag
- US 7,670,425 'Ultra high strength fiber-reinforced cement composition, ultra high strength fiber-reinforced mortar or concrete and ultra high strength cement additives' by Watanabe et al., 2010 [27]: relates to a ultra high-strength fibre-reinforced cement composition containing silica fume and coal gasification fly ash mixed to a specific ratio, gypsum and metal fiber, ultra high-strength fibre-reinforced mortar or concrete containing such a cement composition and fine aggregate, and an ultra high-strength cement additive to be used for such mortar or concrete
- US 7,749,476 'Production of carbonate-containing compositions from material comprising metal silicates' by Constantz et al., 2011 [28]: describes how silicon-based material (eg. slags) and carbonate-containing material may be blended at a later stage to produce a pozzolanic material, which may be further processed and blended with, for example, Portland cement.

4.2.3 PRACTICES IN IGCC SLAG USE

Buggenum

The Buggenum IGCC plant has been in operation since 1998 and has accumulated approximately 80,000 hours of syngas operation. Vliegasonie B. V., a 100% subsidiary of the Dutch electricity producing companies, markets CCPs and has investigated the application of the Buggenum slag as a raw material in cement clinker production. Incorporation of up to 20% slag per ton of clinker in the raw materials was found to be feasible. The cement industry located near Maastricht and Liege enables the use of 150,000–300,000 tons of slag from the Buggenum plant per year.

Wabash River

The Wabash River IGCC Power station was selected in 1991 by DOE as a Clean Coal Technology demonstration project aimed at improving the use of coal as a major energy source. Operation began at the end of 1995, ceasing in December 1999 [29].

Solid by-products from the gasification process at the Wabash facility primarily consisted of gasifier slag, entrained particulates in the syngas exiting the gasifier, and elemental sulfur. The slag from the gasifier was removed in a slag/water slurry and directed to a dewatering system. The dewatered slag was loaded into a truck or railcar for transport to market or a storage site. Clear water from the settled slurry was returned to the gasifier quench section and the slurry of fine particulates from the bottom of the settler was recycled to the slurry preparation area. The entrained particulates were collected from the cooled syngas and recycled to the gasifier. The slag produced was a black, glassy sand-like material, which is considered to be inert on the basis of TCLP leaching tests and therefore need not be treated any differently than coal combustion waste material that is classified as non-hazardous [30].

Consequently, it may be disposed of in a non-hazardous landfill, or sold as an ore for metals recovery. It generally contains 3–10% unconverted carbon and is marketed for asphalt, construction backfill, and landfill cover applications. The slag's hardness also makes it suitable as an abrasive or roadbed material, as well as an aggregate in concrete formulations. Further evidence of the long-term stability of this material is supported in an EPRI publication [31].

The plant also produced 99.99% pure elemental sulfur that left the plant in railcars. It was sold to a broker for agricultural applications, with more than 40,000 tons sold.

Polk IGCC

The Polk power station in Tampa, Florida in the United States, was built and is operated by the Tampa Electric Company (TECO). The IGCC power station was partially funded under the DOE's clean coal technology program [14]. The IGCC facility began commercial operation in 1996 and uses an oxygen-blown, entrained-flow, slurry-fed gasification technology licensed from GE.

Similar to the Wabash facility, solid wastes from the Polk facility consist primarily of gasifier slag and entrained particulates in the syngas. In the gasification system, coarse solids and some fine solids are flushed from the radiant cooler into a concrete slag-dewatering bin. Dewatered slag is then loaded into trucks for offsite use or temporary onsite storage. Water removed is pumped to the gasification process black water handling and processing system. The temporary storage units are designed to provide for up to five years of waste from the IGCC unit operating at 100% capacity.

Particulate removal from the syngas occurs in both the conventional cold gas cleanup unit (CGCU) and a demonstration hot gas cleanup unit (HGCU). The solids from both gas cleanup units are collected as slurry, which is processed in the blackwater handling system. The solids from the slurry are stored at an onsite brine storage area, a lined landfill with a leachate collection system. In the HGCU, sodium bicarbonate is used as a sorbent for halogen removal. A secondary cyclone captures

the injected sodium bicarbonate, which is also sent to the onsite brine storage area. A small amount of non-hazardous sorbent fines are collected in a high-efficiency barrier filter and are sent offsite for disposal. Larger fines are sieved on screens, and fugitive fines are collected in filter bags and recycled to the catalyst supplier.

All blackwater from the gasification and syngas cleanup process is collected, processed, recycled to the extent possible, and contained within the process. The separated water is recycled for slurring the coal feed.

A by-product handling issue reported at the Polk plant is related to the ash/char recycle stream [32]. Polk’s GE gasifier generates char that is mixed with a very fine glassy frit, which requires separation prior to re-injection. The separated frit must be washed with clean water before it can be disposed of economically or used commercially. The Charah process used at the IGCC plant at Polk produces three components:

- coarse slag with a low carbon content
- a medium particle size with a high carbon content, which is used as fuel at the Big Bend power station
- fines with no commercial value, which are recycled to the slurry preparation system.

TECO Energy’s IGCC slag is marketed as ‘black diamond,’ most of which is used to produce cement. TECO provides the slag to a cement manufacture at no cost and subsidises that market by providing shipping costs [33].

Slag not used by cement industry is subject for disposal. Although the slag is classified as non-hazardous, local regulations require disposal in a different class of landfill: Polk must use a Class I landfill that is double-lined with leachate extraction/control, which is more expensive (\$20/ton) than conventional landfill.

Puertollano IGCC

Puertollano power station began operation in March 1998 and was designed with a targeted net electrical output of 300 MW and an electrical efficiency of 45% [34]. It uses a coal blend based on sub-bituminous coal and petroleum coke with a normal weight proportion of 50:50. The amounts of by-products generated during a 10-month period in 2000 are shown in Table 40 [35].

By-product	Amounts, t	%
Fly ashes	7,135	10.5
Slag	52,226	76.5
Filter cake	4,690	6.9
Sulphur (exit)	4,185	6.1

Table 40: Puertollano by-product production in 2000 [17]

With respect to the disposal of solid wastes, ELCOGAS complies strictly with the requirements established in the official solid waste authorisation, sending the vitrified slag to the Encasur coal mine backfill.

The slag from Puertollano plant has been well characterised [36–38] and several applications have been investigated, such as a raw material feedstock for the manufacturing of construction bricks

[39], glass ceramics [40] and lightweight aggregates [38]. Recently, the slag has been valued as a by-product to be used in the fabrication of ceramic products, and it has been agreed to sell the slag to a local ceramic workshops [34].

Fly ashes have been also valued as a by-product to be used as an additive for concrete and are being used by local cement and concrete industries as a component in the manufacture of concrete.

Nakoso power station

Nakoso IGCC power station uses an air-blown, dry-feed, entrained-flow gasifier. Coal slag discharged from the gasifier is considered as inert waste and is suitable for use in land reclamation. This slag can also be used as a substitute material for clay in the cement industry and as a fine aggregate for concrete production [41].

4.3 Summary

These conclusions are made on the basis of current practices in CCP use, which are considered to be applicable for coal gasification residues for the reasons given above. Current and potential applications for IGCC slags include:

- lightweight aggregates
- cement clinker
- cement additive/aggregate
- road base and paving aggregate
- abrasives
- polishing media
- roofing granules
- structural backfill
- mineral filler
- road drainage
- water filtering medium.

Section 6 of this review considers essential characteristics of the slags required for IGCC slags to be used in the most prospective applications in Australia.

Value-added use options for IGCC slags are practically feasible, but could to be limited due to legislative, economical and technical barriers outlined in Section 7.

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5 Current practices for the use of blast furnace and steel furnace slags

5.1 Introduction: blast furnace slag and steel furnace slag applications

Blast furnace slag (BFS) and steel furnace slag (SFS) have a long history of use as industrial by-products, going back almost 100 years in the United States and 150 years in Europe. Ground granulated blast furnace slag (GGBS) has been used in composite cements and as a cementitious component of concrete for many years. The first industrial commercial use (about 1859) was the production of bricks using unground granulated blast furnace slag (GBS). In the second half of the 19th century, its cementitious properties were discovered, and by the end of 19th century, the first cements containing GBS were produced. Since the late 1950s, the use of GGBS as a separately ground material added at the concrete mixer together with Portland cement has gained acceptance. In some countries, the term 'slag cement' is used for pure GGBS [1].

Both BFS and SFS have unique physical and chemical properties that make them particularly well suited to a variety of uses in construction and civil engineering projects [2]. The properties of iron and steel slags can vary greatly, depending on the processing done once the slag is removed from the furnace.

Air-cooled BFS produces a durable aggregate that performs well in unbound applications as well as in Portland cement and asphalt concretes. Cooling the slag with water produces a lightweight aggregate for use in masonry blocks and lightweight concrete. Pelletised and granulated BFS can be ground and used to make slag cement. Compared to regular Portland cement, slag cement provides reduced heat of hydration and improved resistance to sulphate attack and alkali-silica reaction [2]. It is also resistant to chloride penetration, sulphate and thaumasite sulphate attack. It has low risk of thermal cracking and a high electrolytic resistance.

Steel furnace slag typically forms a very angular, durable aggregate that makes it good for use in the transportation industry. SFS has been used successfully in the friction course of hot mix asphalt pavements, as well as in Superpave mix designs and stone matrix asphalt. It is also used as a cost effective and environmentally sound feed stock material for the production of Portland cement.

The main applications of BFS and SFS are [3-5]:

BFS (air-cooled):

- Uncrushed: fill and embankments (particularly areas subject to severe loading, such as mainline rail systems), working platforms on difficult sites pavements, where binding fines are produced by rolling to break the slag down to fill the voids
- Graded road base: on its own or blended with other slags and/or with other natural rocks and sands
- Crushed and graded: for concrete aggregates, concrete sand, glass insulation wool, filter medium, and use under concrete slabs as a platform.

GGBS (granulated BFS) and GGBS:

- Cement: the principal use is as cement replacement (when ground, GGBS), replacing 30–50% of Portland Cement in 'normal' concrete, but can replace up to 70% in specialist applications such as marine concrete. GGBS is probably the most applicable product in the cement industry. For slag cement production, GBS can be ground separately or together with

Portland cement clinker and calcium sulphate [1]. Usually, GGBS is ground to a fineness exceeding that of ordinary Portland cement to obtain an increased early strength.

- Aggregate: unground GBS is suitable as a normal weight aggregate in concrete.
- Road making: unground GBS can be used as a base layer material in road construction.
- Fill material: because of its sand-like texture, it is easy to work. Its self-cementing properties cause it to set up over time.
- Sub-base: GBS compacts more readily than rock slag (air-cooled BFS). Initially, the compacted surface of this material is soft, but it hardens with time. Granulated blast furnace slag can have up to 99.5% reactive glassy material, which accounts for its self-cementing properties.
- Stabilising binder: one of the major benefits of using slag products in a stabilised pavement is the slow rate of the cementation process. The pavement material can be reworked up to two days or more after initial mixing depending on the binder, without reducing the final strength. The performance of both GBS and GGBS in stabilisation depends on the degree of fineness of the material, which in turn is a matter of economics. The cost of producing a finer grade of both GBS and GGBS, coupled with the reduced amount of slag stabilising binder needed to provide equivalent strength, must be balanced against haulage costs. Blends using slag, fly ash and lime have working times up to four times that of GP cement with working times of up to 48 hours being available with some soils [6].
- Other uses include glass making, concrete block manufacture, sporting field sub-base (for drainage), filtration medium, reinforced earth embankments, and mine backfilling and grit-blasting medium requiring fine etching.

BOS (basic oxygen steel slag):

- Blending with many other products such as granulated slag, fly ash and lime to form pavement material
- Other uses include skid-resistant asphalt aggregate, rail ballast asphaltic concrete aggregate, soil conditioner, hard stand areas and unconfined construction fill.

EAF (electric arc furnace slag):

- Blending with many other products, such as granulated slag, fly ash and lime, to form pavement material, skid-resistant asphalt aggregate and unconfined construction fill. SFS is most commonly used for asphalt application, as it has better strength, abrasion and impact resistance than BFS, making it particularly suitable for use in areas subjected to heavy vehicle loads and high shear.

As silicate liming materials, SFS and BFS contain elements with useful properties for plant nutrition and soil quality [7]. The basicity of the calcium and magnesium compounds in the slags improves soil pH. Both elements also serve as plant nutrients and stabilisers for soil aggregates. Magnesium in slags (especially in BFS) has a better solubility than that of magnesium carbonate in limestone and dolomite. Silicate has beneficial effects on plant health, phosphate availability and soil structure. The content of trace elements, such as manganese, copper, zinc, boron or cobalt, satisfies both plant and animal demands [8, 9].

Iron and steelmaking slag manufacturing processes and the applications are summarised in Table 41.

Common nomenclature	Manufacturing process	Applications
Blast furnace slags		
Air-cooled BFS	Crushing and screening slag that has been slowly cooled. Also available as uncrushed slag, i.e. spalls or skulls	Road base/sub-base, concrete aggregate, filter aggregate, construction/selected fill, scour protection, rockwool
GBS	Rapidly quenched molten slag with high pressure, high volume water spray	Road sub-base, construction fill, construction sand, stabilising binder, cement manufacture, grit blasting, reinforced earth wall infill, glass manufacture
GGBS	Grinding granulated slag to cement fines	Cement replacement, stabilising binder
Pelletised slag	Water quenched molten slag on a sloped table and rotating drum, which throws the pellets into the air for further cooling	Cement manufacture, lightweight aggregates for masonry products and structural concrete
Lightweight slag	Controlled cooling of slag as a thin layer in a pit, followed by crushing and screening	Skid-resistant aggregate, lightweight aggregates for masonry products and structural concrete
Steel furnace slags		
BOS	Crushing and screening slag which has been air cooled and watered	Sealing aggregate, asphalt aggregate, road base/sub-base, construction fill, subsoil drains, grit blasting
EAF	Crushing and screening slag which has been air-cooled and watered	

Table 41: Manufacturing processes and applications for iron and steel slags [4]

5.2 Current practices in Europe

In Europe, BFS and SFS are used in large quantities of about 25 million tons and 17 million tons, respectively [10]. Both types of slags are mainly used in the development of infrastructure such as roads (aggregates/asphalt), buildings (cement/concrete) and fertiliser.

In 2004, about 23% of BFS was processed as air-cooled slag and 77% as vitrified slag (granulated or pelletised). Most European countries produce both air-cooled and GBFS. In some countries (Belgium, Italy, The Netherlands) only GBFS is produced, while in Sweden and Spain the main product is air-cooled slag. The dominant application is the production of slag aggregates or slag mixtures for unbound or self-binding layers: this accounts for about 64% of generated BFS, most of them granulated or pelletised. About 33% of generated BFS, mainly air-cooled BFS, is used for road construction. Due to their porosity, BFS aggregates are today only used for asphalt road bases and sub-bases, but not for surface layers. Other applications of BFS include interim storage (1.5%), internal recycling (0.4%), hydraulic engineering (0.3%) and fertiliser (0.2%) [10].

SFS produced in 2004 was as BOF slags (~62%), EAF slags (29%) and secondary metallurgical slags (~9%). The use rate of SFS is lower than BFS: approximately 11% of the steel slags produced in Europe today are still being dumped. The main areas of SFS application are in the production of aggregates for road construction (45%; asphalt layers, in-situ treatment of unsuitable soils for road construction). Other applications include: interim storage (17%), internal recycling (14%), the production of fertiliser (3%) and hydraulic engineering (3%). Only 1% is used for cement production [10].

The overall usage of BSF and SFS, based upon more recent data, is shown in Figure 1.

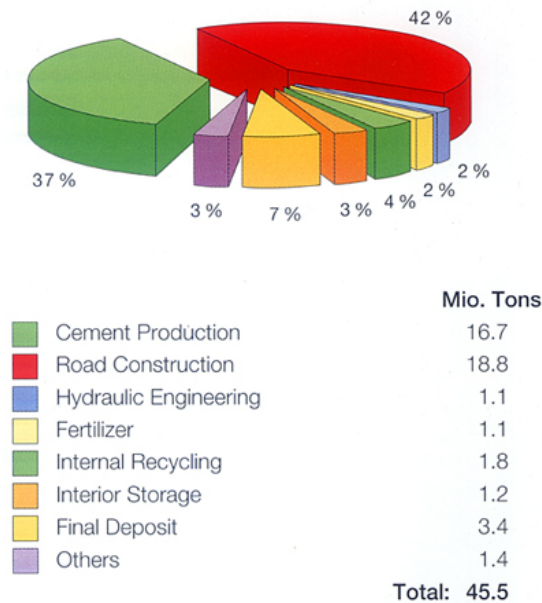


Figure 1. Distribution of BFS and SFS in Europe

Both the chemical and physical characteristics of BSF and SFS are quality controlled as a result of voluntary operations and treatment both before and during slag production. Quality control is maintained by controlling the characteristics of raw materials, the use of chemical additions (e.g. aluminates in the furnace), cooling rates, etc. to fulfil the requirements of nationally and internationally recognised technical and environmental specifications and standards.

Recently, most of the national standards relevant to slag use have been harmonised. In the European cement standard EN 197-1, nine cements containing between 6 wt.% and 95 wt.% slag are listed. It also contains requirements for glass content and basicity of GBS. The oxide composition of GBS may be used as a guide to possible reactivity. However, investigations have shown that the evaluation of GBS based only on the chemistry or any other single parameter does not give entirely reliable results [1]. The interaction of the slag with Portland cement clinker, calcium sulphates and other materials, as appropriate, has to be considered.

In Europe, severe legal limitations have been put on the Cr(VI) content in cement. Under the EU Directive 2003/53/CE, hydrated cement must not contain more than 2 ppm of soluble Cr(VI) in the dry cement mass. Hence, BOF slag now cannot be used as a raw material, as 10% of the total Cr injected in the kiln is Cr(VI) [11]. However, for BFS slags, Cr(VI) content is not an issue. As shown in Section 3, the concentration of Cr in BFS slags is thousands of times lower than in BOF slags, and Cr leaching is 2–3 orders of magnitude lower.

For each intended field of application, slag must meet the same standards of health and environmental protection as those applicable to primary raw materials and products. In this regard, some slag products are superior to their natural equivalents.

5.3 Current practices in the United States

Details of recent use practices for BFS and SFS in the United States were recently published [12, 13]. The United States consumed approximately 21 million tons of domestic iron and steel slag in 2005, 60% of which (12.6 million tons) was BFS [14].

5.3.1 BLAST FURNACE SLAG USE

Most of the BFS produced in the United States are air-cooled slags. The supply of GBFS from domestic blast furnaces is constrained by limited facilities with granulation cooling. Such facilities are currently installed at only five blast furnaces in the United States, and one of these has been idle since mid-2005, with no assurance of restarting [12]. Retrofitting other blast furnaces with granulators is possible and a handful of new slag grinders are being constructed in the United States, which will likely increase GGBFS supply in coming years (EPA 2008).

BFS aggregates are used as a substitute for virgin aggregate in road base, concrete, asphalt concrete, rail ballast, roofing, shingles, mineral wool and glass making. GGBFS is used as a supplementary cementitious material. SFS is used within the agricultural industry or as water filter media for acid mine drainage and pollution control [15].

A preliminary sampling of three BFS processors in the United States has identified approximately 100 million metric tons of stockpiled slag as of 2006 [8]. The total quantity of stockpiled slag in the United States is likely to be significantly higher, since some of the slag processors have not been surveyed. Some of the stockpiled material is mined from slag piles at closed iron and steel plants [15].

Table 42 demonstrates generation and usage of BFS in the United States in 2004.

	Annual quantity generated	Annual quantity used as Cement kilns	Annual quantity used as others	Annual quantity landfilled	Annual quantity	Total quantity stockpiled (2006)
BFS, Mt	12–14	0.25	0	0	11.58	>100

Table 42: Overview of generation and use of BSF in the United States in 2004 (millions short tons) [12]

5.3.2 STEEL FURNACE SLAG USE

The generation of steel slag from integrated iron and steel works is in significant decline, owing to the idling of several plants and an increasing trend of returning slag to the furnaces. In contrast, slag from electric arc steel furnaces (largely fed with steel scrap) is still being produced in significant quantities [13].

As for BSF, SFS is often used as a raw material substitute in cement clinker manufacturing and concrete [15]. Steel slag is useful as an aggregate in granular base applications, and is also used as an aggregate in embankments, engineered fill and highway shoulders [16].

SFS can also be used for remineralisation in the agricultural industry, and as a water filter media for acid mine drainage and water pollution control. Basic oxygen furnace steel slag is an effective material for use in permeable reactive barrier systems for the removal of phosphorus and pathogens such as *E.coli* from groundwater and wastewater [17].

Table 43 shows the breakdown of United States SFS sales across different applications from 2004–08 [13, 18].

Use	2004	2005	2006	2007	2008
Asphaltic concrete	12.9	15.6	12.1	14.4	10.9
Road bases and surfaces	63.5	53.0	51.0	51.5	60.3
Fill	9.6	10.5	17.9	13.3	10.8
Clinker raw material	5.5	6.9	6.9	6.7	5.0
Miscellaneous	2.9	2.3	0.8	2.3	0.5
Others/unspecified	5.6	11.7	11.3	12.0	12.7

Table 43: Overview of SFS sales in the United States in 2004-2008, %

No data are readily available on the disposal of BFS and SFS, but it is likely that the use of steel and blast furnace slags is nearly 100% of United States production, in which case disposal is minimal.

5.4 Current practices in Asia

5.4.1 CHINA

GGBS is the dominant by-product from the iron and steel industry in China: 49 modern slag grinding plants produced 31.2Mt of GGBS in 2007 [19]. Similar to other countries, China has used its increased amount of GGBS mainly as clinker substitution in blended slag and normal cement production, and as supplementary cementitious material in ready-mixed and site-batched concrete production. This accounts for 73% and 27% of the total GGBS output, respectively. Due to the lack of unified national standards and technical guidelines for use of GGBS in durable concrete structures, a very low amount (5–8%) of the total GGBS output is estimated to be used for concrete production, mostly due to the requirement of durability.

Most steelmaking slags are used as construction materials, mainly as sand and coarse aggregate. Some research has been conducted in the use of slag as a fertiliser and soil additive; however, only a few components, such as CaO, MgO, SiO₂ and P₂O₅ were used [20].

5.4.2 JAPAN

About 35–40 million tons of blast furnace and steelmaking slags are generated in Japan annually, and about two-thirds of that is BFS. Table 44 shows the production and use of BFS in Japan in 2008–10 [21].

GBS constitutes about 75% of the total BSF produced in Japan and is mainly used in cement applications, while air-cooled slags typically are used in road applications. On average, more than 95% of BSF produced in Japan is used.

Year	Slag type	Produced, metric kilo tons	Uses, metric kilo tons						% used
			Road	Cement	Soil improv.	Civil	Concrete aggregate	Other	
2008	Air-cooled	4,094	3,557	312	29	128	295	333	
	GBS	21,003	164	15,638	110	1,117	2,390	196	
	Total	25,437	3,740	15,950	139	1,245	2,686	529	95.5
2009	Air-cooled	4,124	3,133	272	13	126	250	313	
	GBS	17,551	121	14,153	387	567	1,785	206	
	Total	21,675	3,254	14,425	400	693	2,035	519	98.4
2010	Air-cooled	5,085	3,230	178	16	218	272	449	
	GBS	19,839	138	15,511	438	1,207	1,688	220	
	Total	24,924	3,368	15,689	454	1,426	1,959	669	94.5

Table 44: Production and use of BFS in Japan in 2008–10

JFE Steel has been involved in the development of various new uses for slag. Some of the developments were started by research and development departments and technology centres under Kawasaki Steel Corporation and NKK Corporation before the two steel makers merged in 2003 [22].

5.5 Current practices in Australia

During 2000, approximately 3.1 million tons of iron, steel and other slags were produced in Australia and New Zealand. The major regional centres are Port Kembla and Whyalla for BFS and SFS. EAF steel slag is produced in smaller quantities at Melbourne, Sydney and Newcastle [14]. Of the 3.1 million tons of slag produced in 2000, 75% was used. The major contributors to this increase were GBFS at 100%, BFS at 71%, BOS at 64%, EAFS at 54% and other slags at 24% [4].

BFS and steel slag products and their applications in Australia are described elsewhere [4, 5]. Examples of the applications and guides to slag use in Australia are presented below.

5.5.1 ROAD BASE/SUB-BASE

Road base application is suitable for BOS, EAF and air-cooled BFS. GBS can be used in sub-bases only. Slag is a versatile self-cementing material that can accommodate various activators to improve the cementing action. Non-cementitious materials can also be accommodated if the cementing action needs to be suppressed. The French Road Authority, SETRA, has developed a group of slag pavement types called 'gravel slag' using granulated slag as a binder with hydrated lime as an activator [23]. Several of these blends have been trialled in Australia, and test information is available [24]. Detailed guidance on the properties and use of BOS and EAF slags in asphalt and sprayed seals may be obtained from the Australian Slag Association (ASA)'s publication 'A Guide to the Use of Steel Furnace Slag in Asphalt and Thin Bituminous Surfacing' 1999 [25]. Detailed guidance on the selection of road surfacings may be obtained from the Austroads publication 'Guide to the Selection of Road Surfacing' 2000 [26].

5.5.2 BLAST FURNACE SLAG CONCRETE AGGREGATES

BFS aggregates are available in a full range of sizes and blends, as required for concrete manufacture. Detailed information on the properties and use of blast furnace slag in cement and concrete is provided in the ASA's publication 'A Guide to the Use of Iron Blast Furnace Slag in Cement and Concrete' 1997 [5].

In 2002, more than 450,000 tons of slag aggregate and slag sand was used by the concrete industry. Some examples of slag cement and aggregate applications include:

- Sydney Harbour Tunnel: The cement for the immersed tube segments comprised 40% ACSE (Shrinkage limited) cement with 60% GBFS, interground with optimised gypsum content. Approx. 36,000 tons of cement was used for these units.
- Anzac (Glebe Island) Bridge, Sydney: The two pile caps supporting the towers for this cable-stayed bridge used high-slag cement as used in the Sydney Harbour Tunnel. Each of the caps contained approx 2,800 m³ of concrete, which was continuously poured.
- Maribyrnong River Bridge: This bridge has a total length of 520 m (54-m spans) and was constructed using an incremental launch system. The construction method allowed segments to be placed at one end and subsequently launched (jacked) into position on a weekly cycle. It used slag cement 70% OPC, 30% slag and 20,000 m³ of concrete.

More examples of application of the BFS concrete aggregates could be found in [4].

5.5.3 CONCRETE WITH SLAG-BLENDED CEMENT

BFS has a chemical composition similar to Portland cement, although in different proportions. GBSF satisfies the requirements of Australian Standard AS3582.2 Supplementary Cementitious Materials for Use With Portland Cement, Part 2 [27]. Slag-blended cement meets the requirements of Australian Standards AS3972 Portland and Blended Cement.

Concretes made with slag-blended cement have excellent flow characteristics, particularly where vibration is employed. The setting time for blended cements may be longer than for Portland cements, particularly in cooler temperatures, due to the slower initial rate of reaction between the GGBS and water, compared with that of Portland cement. However, slag-blended cement develops strength more rapidly than GP cement. Examples of the use of slag-blended cement in concrete include [4]:

- Sydney Harbour Tunnel submerged tube units: Cement contained 60% ground granulated blast furnace slag

- Pile Cap Foundation Blocks for the Anzac Bridge, (Glebe Island Bridge), Sydney. Cement contained 60% GGBFS
- GGBFS and fly ash used as a blended cement in Yandina Bypass on the Bruce Highway in Queensland
- High slag blend 65/35 used in lift wells for Colonial Stadium Melbourne to reduce heat of hydration and thermal cracking
- Sydney Airport Link Tunnel used high slag-blend cement for high acid soil environments
- Floating oil platforms used high slag-blended cement for chloride resistance.

5.5.4 ENVIRONMENTAL BENEFITS

The use of slag in cement substantially reduces the generation of greenhouse gases, with a reduction of one tonne of CO₂ discharged into the atmosphere for every tonne of slag substituted for GP cement in the production of blended cement [4]. The use of rock slags conserves the energy already expended in their production and also conserves our finite natural resources.

5.6 Summary

Both BFS and SFS have physical and chemical properties that make them particularly well suited to a variety of uses in construction and civil engineering applications.

In many countries, more than 95% of blast furnace and steel making slags produced are used. IGCC coarse slags have many similarities to GBS slags, and therefore may have similar applications and use rates. However, more research is required to fully characterise IGCC slags to identify their suitability for these potential applications. This will be discussed in more detail in Section 6.

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6 Utilisation options for IGCC slags and fly ashes in Australia

6.1 Introduction

As discussed in previous sections, IGCC solid residues mainly consist of raw slag, which includes coarse slag or frit (vitrified coarse fraction) and fly slag [1]. Most of the potential applications of IGCC slags reflect the experience of use of slags from other industries (eg. iron and steelmaking slags) and also, where applicable, use of fly ash and boiler slags.

Depending on the application, IGCC residues will have to meet certain criteria according to Australian standards to be used in Australia. The following sections consider separately each case for potential IGCC by-products. Selection of the specific use concepts should be guided by the following criteria:

- similarity between the properties of slag and those of the material it replaces
- achievement of comparable final products meeting the necessary functional requirements.

6.1.1 SLAG CEMENT AND SLAG/FLY ASH BLENDED CEMENT IN CONCRETE

The Building Code of Australia defines requirements for building regulations in Australia. According to [2–4], fly ash or slags have to be compatible with:

- Admixtures that comply with AS 1478 Chemical Admixtures for Concrete
- Fly Ashes complying with AS 3582.1 Supplementary Cementitious Materials for Use with Portland cement: Fly Ash
- Ground granulated blast furnace slags complying with AS3582.2 – Supplementary cementitious materials for use with Portland cement
- Amorphous Silica complying with AS3582.3 – Supplementary cementitious materials for use with Portland cement: Amorphous silica
- Portland and blended cements complying with AS3972 – Portland and blended cements.

Table 45 details the relevant specified requirements of AS3582.1 and the typical values achieved by fly ash [4] and IGCC residues. All testing is conducted in accordance with the relevant Australian Standard test methods, at a National Association of Testing Authorities-registered laboratory.

Property		AS3582.1	Typical Fly ash Tarong	IGCC fly ash	IGCC slag
Fineness Passing 45- μ m Sieve	Min	75	≥ 85	≥ 80	To be milled
Loss on ignition	Max	4.0	≤ 2	2–24	0.1–24.2
Moisture content	Max	1.0	≤ 0.1	0.4–3.1	<0.1–0.6
SO ₃ content, %	Max	3.0	≤ 0.2	1.3–2.1	0.05–0.45

Table 45: Properties of fly ash and IGCC residues to comply with AS 3582.1

Section 3.3 gives examples of compositions of IGCC by-products. IGCC fly ash has up to 3% moisture after filtration and therefore would require further drying to satisfy AS 3582.1. Loss on ignition (LOI) values of slag and fly ash samples obtained from pilot-scale testing of Australian coals are variable: two of the tested samples have very low LOI values, with other samples having values up to 24% LOI. This variation is significant, as it illustrates the importance of coal-specific conversion characteristics and slag behaviour under variable gasification conditions, and suggest that some residues would require beneficiation to comply with AS3582.1.

Slag cement currently available in Australia contains 20–40% slag for general construction and 60–70% slag for applications that require reduced heat of hydration and increased resistance to the ingress of chloride and sulphate ions, and to inhibit alkali-aggregate reactions [2].

AS 3582.2 sets out the requirements for GGBSF as a supplementary cementitious material in cement and mortar. IGCC slag has to be milled to meet these requirements to be used as supplementary cementitious material.

6.1.2 SLAG IN CONCRETE AGGREGATES

Slag aggregate should not be directly substituted for other aggregates in an existing concrete mix [2]. Rather, a mix should be specifically designed based on slag characteristics (e.g. density and adsorption). Desired characteristics include:

Size: IGCC slag would have to be crushed and screened to a full range of aggregate sizes.

Water absorption: Similar to BSF slags, IGCC slags are vesicular; the individual pieces of slag contain unconnected voids occurring throughout the slag and appearing as blind holes on the surface [2]. It is important that the moisture content around the saturated surface dry conditions is maintained while the slag is in storage awaiting batching. There is no maximum value for water absorption stipulated for any aggregate, including slags [2], and the water absorption of aggregates can vary considerably without affecting many of the properties of the resulting concrete.

Particle shape: The proportion of misshapen particles shall not exceed 10%. For example, air-cooled BFS has less than 3% of these particles than tested to AS 141.14 at a 3:1 ratio [2].

Wet strength: AS 2751.1 specifies the Wet/Dry Strength Variation test as a true guide to the durability of slag aggregates [2]. AS 2758 permits values other than those listed in Table 46 for wet strength and Wet/Dry Strength variation when vesicular aggregates are considered. Hence, these tests are not as critical for assessing the suitability of IGCC slags from Australian coals.

Concrete grade	Nominal max size, mm	Water absorption, %	Wet Strength, kN	Compressive Strength, MPa, for various mixtures		
				7 days	28 days	91 days
50	10&20	4–5	75–95	35–47.5	53.5–64.5	Not cast
60	10&20	4–5	75–95	47–57.5	63–74	Not cast
High strength	7	3–4	80–100	102.5	117.5+	119
	10	4–5	75–95	84–86.5	84–114.5	107–117
Test method		AS 141.5&6	RTA–T215			AS 1012.9

Table 46: Comprehensive strength of slag aggregate in concrete mixes

Los Angeles value: This test reflects the toughness of the aggregate particle. There is no set value for assessing slag suitability; numbers that are known to be suitable are used based on previous experience with the application [5].

Sodium sulphate soundness: Slag aggregates should have a high degree of resistance to sodium sulphate attack (when contacted with sea water or certain ground waters). Maximum sodium sulphate soundness losses for particular concrete exposures are listed in Table 47 [6].

Concrete exposure classification	Maximum weighted average loss, %
Severe	6
Moderate	9
Protected	12

Table 47: Sodium sulphate soundness in concrete aggregates (AS 1141.24 ,AS2758.1)

Chloride and sulphate content: After processing, slag aggregate has to have chloride and sulphate ion contents comparable to natural aggregates. Concentrations are measured according to AS 1012.20 [7]. Corresponding levels of chloride and sulphite ion natural aggregates are 20–460 ppm and 10–1450 ppm respectively.

Bulk density: there are no standard values for bulk density of slag aggregates. BFS slags have bulk density for 20mm aggregate, as follows:

- Loose: 1200–1300 kg/m³ (RTA test method T211)
- Compacted: 1300–1400 kg/m³ (RTA test method T212), which are lower than those for natural aggregates [2].

IGCC slags would have to comply with these values.

Alkali-aggregate reaction: Alkali-aggregate reaction results from alkalis in the cement reacting with certain type of silica or carbonate compounds contained in some aggregates, which leads to expansion and cracking in concrete [2].

AS 1141 lists Method 39 as a means of recognising aggregate that may be alkali reactive [8]. According to this test, BFS slag aggregates are classified as ‘innocuous’, as far as alkali aggregate activity is concerned [2]. The alkalinity of gasification slags is likely to be more variable than found for BSF slags, meaning that each slag may have to be individually assessed.

Iron unsoundness: This may occur as disintegration of the slag when immersed in water. It is likely to become a problem when the slag contains more than 3% of ferrous oxide and at least 1% of sulphur. AS 2758 notes that iron unsoundness has not been recorded for Australian BFS [9]. Since sulphur content in IGCC slags from selected Australian coals have been found to be less than 1%, it is likely that iron unsoundness would not be an issue for IGCC slags.

The properties and characteristics of BFS and the required characteristics of IGCC slags from Australian coals are summarised in Table 48. The most significant feature of this table is that very little is known of IGCC slag characteristics, identifying the need for further research to identify potential use options.

Property	BFS values [24]	BFS rating [24]	IGCC slag values	IGCC slag rating
Water absorption	3–6%	Medium to high	TBD	
Particle shape	3% misshaped	Cubic	TBD	Cubic*
Wet strength	75–100kN	Low	TBD	
LA abrasion value	N/A	High	N/A	
Sodium Sulphate soundness	1% loss	Sound	TBD	
Chlorine content	20–460ppm	Low	40–300ppm	Low
Sulphate content	0.001–0.033	Low to medium	TBD	
Alkali/aggregate reactivity	No	Innocuous	TBD	
Drying shrinkage	–	Low	TBD	
Flexural strength potential	–	Adequate	TBD	
Suitability for pumping	–	Adequate	TBD	

Table 48: Slag properties in slag concrete aggregates. *Crushed slag

6.1.3 ROAD CONSTRUCTION APPLICATIONS

Asphalt and spray sealing

Detailed guidance on the properties and usage of BOS and EAF slags in asphalt and sprayed seals may be obtained from the ASA’s publication *A Guide to the Use of Steel Furnace Slag in Asphalt and*

Thin Bituminous Surfacing [10] and the Austroads publication *Guide to the Selection of Road Surfacing* [11].

Asphalt concrete hot mixes containing varying concentrations of asphalt and 30–50% slag by weight as the fine aggregate were tested for their strength (S-values) in a laboratory. A mix in which 30% slag was combined with 6% asphalt yielded an S-value of 50, which is much higher than the minimum value of 30–37 required for various grades of asphalt concrete. This mix, which had good workability, compares favourably with the standard test mix containing 5% asphalt, with an S-value of 50 [12].

SFS is most commonly used, as its better strength, abrasion and impact resistance than BFS make it particularly suitable for use in areas subjected to heavy vehicle loads and high shear stress [13]. Given the similarities between blast furnace slags and gasification slags, use of IGCC slags in asphalt and spray sealing applications may be less feasible than in other use schemes.

Pavement

Materials considered for use in pavements require the following broad characteristics [14]:

- workability
- strength (both as a matrix and individual particles)
- durability
- stability
- value for money.

In addition, pavement materials must meet the pavement design criteria to ensure adequate performance. These criteria relate to the elastic properties of materials, which govern the distribution of loads throughout the pavement structure, and also the fatigue performance of bound materials, which determines the service life. Unbound materials develop shear strength through particle interlock and have no significant tensile strength.

Both blast furnace and steel slags have <5% misshapen particles, with a calliper ratio of 3:1 indicating good particle shape. This ensures good packing of the particles and facilitates compaction. The vesicular nature of slag particles also promotes good particle interlock and high shear strength [14].

The use of IGCC slag in road construction was studied by testing various asphalt mix designs incorporating slag. By itself, the slag was not found to be suitable for surface pavement applications, due to the lack of coarse particles and the tendency to degrade when abraded [12].

Stabilisation

To satisfy structural pavement design requirements for heavily trafficked roads, where the stabilised layers are the primary load-bearing layer, stabilised layers of at least 300 mm thickness with a modulus value of at least 5,000 MPa are usually required [14].

Binder suppliers began making slower setting binders containing combinations of granulated ground blast furnace slag, lime and fly ash, which could be individually designed to meet the requirements of the material being stabilised and specific job conditions. These binders have significantly longer setting times than Portland cement, which allows adequate compaction and shaping of the stabilised layer to occur. In addition, they generally have improved shrinkage properties compared with Portland cement, which allows the formation of a shrinkage cracking pattern of much finer cracks that do not adversely affect subsequent pavement performance.

A detailed discussion of cementitious stabilisation is provided in Austroads 'Guide to Stabilisation in Roadworks' [13].

Laboratory testing is normally carried out to determine the quantity and type of binder required to meet design requirements for particular materials. The 7-day accelerated Unconfined Compressive Strength (UCS) is commonly used for this purpose. It should be noted that the result will only reflect a portion of the long term in-situ strength. Cores taken from the field after 9 to 12 months have been shown to be often two or three times greater than the 7-day accelerated UCS value obtained. Guidelines for laboratory testing procedures are described in Austroads [15] and have to be applied for testing gasification slags for this application.

6.2 Summary

As with BFS, the most immediately prospective application of IGCC slags from Australian coal would appear to be in the cement industry and some road base applications. It is important to apply the requirements for slag use in terms of their technical (including physical and chemical) characteristics, rather than simply assess their suitability on the basis of the bulk analysis or the industry of origin.

Preliminary investigations in the United States that indicate that gasification slags may have a potential use as a cement additive. However, considerably more research is required to establish that the slags meet the stringent standards required for many of these potential applications.

Slag characteristics are likely to be influenced both by feed coal properties and gasifier operation. This may affect properties such as unburnt carbon levels, high concentrations of which would severely limit potential applications.

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7 Knowledge gaps in an Australian context

7.1 Classification of wastes and environmental regulations

Traditionally, government regulations specify ash as a waste rather than a product. The descriptor of CCP is commonly used in the industry to avoid the term 'waste'. More recently, some international and Australian regulators have promoted CCP exemption from classification as waste. For example, in Queensland, CCPs are defined as a 'resource for beneficial use' rather than a waste. Although many states are encouraging waste minimisation and recycling, no regulations currently exist that encourage the beneficial use of CCP.

Regulatory uncertainty exists concerning the environmental effects of ash disposal options [1]. For disposal schemes, some types of waste require further classification to assess and determine the total and leachable trace element concentrations. Ambiguity also exists where state regulations use the same terminology for classification of wastes, but set differing limiting values on the definitions. The National Waste Policy Implementation Plan attempts to introduce a national definition and classification system for waste that is in accord with definitions in international conventions.

Recently, the EPA has stipulated a Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption under Part 6, Clause 51 and 51A. This is the coal ash exemption 2011 effective as at 14 June 2011 [2]. It is likely that state regulations will incorporate these changes in national regulations on ash and other CCP by-products.

Initial data on the leaching behaviour of gasifier slags derived from Australian coals suggest that they are unlikely to face any legislative barriers to their disposal or use. However, the influence of feed coal characteristics and gasifier operation on leaching behaviour of the slag is largely unknown, and needs to be determined to ensure that the appropriate environmental and legislative requirements can be met. Acknowledgement of the role of properties, rather than the origin of the waste, is essential for proper positioning of gasification by-products in Australian regulations.

7.2 Environmental characterisation of wastes

The wide range of leaching tests commonly in use have already been discussed in some detail (Section 3.2). The use and relative merit of these tests has been the subject of extensive debate in the literature, which has also been reviewed in Section 3.2. Scott *et al.* reviewed leach methodologies from an Australian perspective and concluded that TCLP was limited in its usefulness as a regulatory tool in Australia [3]. The ASLP allows 'waste type' and 'disposal situation' to be included in the decision process. Most (but not all) of Australian states use ASLP leaching tests for classification of waste and waste management schemes. Many of the leaching tests, such as the TCLP, were developed for the testing of municipal waste and may not be applicable to the proper assessment of CCP leaching behaviour.

Further research is required to determine the most appropriate leaching test, taking into consideration not only the characteristics of the waste material, but also the environment in which it will be disposed of or the potential end use.

7.3 Potential use barriers for gasification by-products

It is in both the community's and the generators' best interests to reduce the quantity of ash sent to waste impoundments of all categories, and to increase the amount directed towards productive

streams [4]. However, there are existing constraints to ash use, which likely expand to other coal use by-products, such as gasification slag:

- Extraction and transportation of ash to cementitious product users; this tends to be mostly applicable only where generators are in proximity to the plants using the material [5]
- Markets for use of the material must be adequate and of feasible proximity
- Lack of responsibility by coal producers for their product due to ash not being a core product [5]
- Competition between ash producers [5]
- Vertical integration of the cement, concrete and quarrying industries, which limits the use of by-products [6]
- Regulation concerning the use of ash in applications such as fills and agriculture
- Availability of required quantities of consistent, high-quality coal fly ash meeting the specifications for use in concrete [6].

The most commonly referenced consideration in terms of barriers to ash use is the cost of transport. Transportation of ash is neither difficult nor technologically challenging. However, ash is fine and prone to dust emissions, which may require some form of moisture control; this adds to transportation costs. Since slags from entrained flow gasification are granular and denser than fly ash, they are likely to pose less of a concern with fugitive dust. However, transportation costs are still likely to be a potential economic barrier.

Other obstacles for potential slag use are related to specific slag characteristics, which may include:

- Pores within the slag may affect material bulk density, which is not accepted in product specifications
- High unburnt carbon content, which would limit its use in cement/concrete applications
- Variation in the shape, size and friability of the slag, which could affect its use in road base and as aggregate
- High alkali content of the slag would exclude its use in cement/concrete applications
- Some of trace element content can exclude CCP products from viability for some uses
- Limited knowledge of the characteristics of slag derived from Australian coals and the influence of gasifier operating characteristics on slag properties.

To overcome these barriers and create successful use strategies for gasification slag, its potential use needs to be demonstrated to be technically safe, environmentally sound, socially beneficial and commercially viable. Very little data is currently available to address these concerns. Therefore, a research program is required to provide the necessary data.

7.4 Availability of gasification by-products

There is only limited knowledge of characteristics of slags from gasification of Australian coal. This is due to the absence of full-scale or large pilot-scale gasifiers in Australia, and the challenges associated with sourcing slags from other pilot-scale gasification operations. Where possible, this review has discussed characteristics of gasification by-products from Australian coal, using the limited number of samples obtained from some recent research programs. However, these outcomes cannot cover the range of Australian coals and the gasification technologies in which they may be used. There is a clear need to have a representative database on coal slag characteristics, which includes specific feed coal characteristics and the influence of gasifier technology and operating conditions.

One of the approaches taken in the project is explore the possibility of extending the database of slags from Australian coals by reproducing the slags in laboratory conditions as similar as possible to industrial conditions. Initially, the validity of this approach will be tested by conducting the

laboratory experiments using coals that have previously been tested in a pilot-scale gasifier and for which data is available. If this approach is shown to be valid, it will be a cost-effective way to quickly build up a database of slag characteristics that can be used to assess potential applications.

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8 Concluding remarks and recommendations

8.1 Summary

This review has provided an assessment of available data, experience, regulations and outcomes pertaining to existing international IGCC projects, international coal gasification-based chemical industry practices, and other relevant technologies, such as iron and steel making. This information has been presented in the context of current practices for management of solid wastes from existing coal combustion-based processes.

While IGCC by-products are not specifically mentioned in any Australian legislation, they are likely to be assessed in the same manner as coal combustion products, such as fly ash and bottom ash. If so, then they will be classified as a waste, rather than a resource. However, as with coal ash, there do not appear to be any specific legislative barriers to reuse. There is also a move away from a prescriptive approach to a 'fit for purpose' approach, although this is in very early stages (e.g. recent Queensland legislation). Much of the current legislation is based more upon international legislation, and lacks a sound scientific basis. As shown in Section 2.7, state and territory legislation varies considerably. A more uniform, national approach based on sound scientific information is required.

This review examined the potential barriers to use, based upon the similarity of gasification slag to other coal combustion products. The following potential barriers were identified:

- Community acceptance of increased coal combustion product use in community products needs to be obtained for more widespread integration into fields such as engineering materials and agriculture.
- Generators must view ash as a product, and not as an inconvenience or waste material.
- Markets must be made aware of the potential use and the benefits of the product.
- Legislation and standards must be introduced into the market so that end users are comfortable with the viability of the material in place of traditional materials. However, current legislation is supportive of coal combustion product use schemes, and any introduction of carbon taxes or waste disposal taxes would increase the viability of IGCC by-product use.

Value-added use options are technically feasible, but are likely to be limited, due to the small size of the potential Australian market.

Gasifier slags have similarities to both blast furnace and steel furnace slags. Gasifier slags are therefore likely to have physical and chemical properties that suit them particularly well to a variety of uses in construction and civil engineering applications.

In many countries, more than 95% of blast furnace and steel making slags are used. Given their many similarities to granulated blast furnace slags, gasifier slags therefore may have similar applications and use rates. However, more research is required to fully characterise IGCC slags to identify their suitability for these potential applications. This will be discussed in more detail in Part II of this report.

Based upon their similarities to pf coal combustion by-products and furnace slags, potential applications for IGCC slags include:

- lightweight aggregates
- cement clinker
- cement additive/aggregate
- road base and paving aggregate
- road drainage

- abrasives
- polishing media
- roofing granules
- structural backfill
- mineral filler
- water filtering medium.

Preliminary investigations in the United States indicate that gasification slags may have a potential use as a cement additive. However, more research is required to establish that the slags meet the stringent standards required for many of the potential applications. Slag characteristics are also likely to be influenced by feed coal properties and gasifier operation. This may affect unburnt carbon levels, high concentrations of which would severely limit potential applications.

Knowledge of slag characteristics from gasification of Australian coal is limited. This is due to the absence of full-scale or large pilot-scale Australian gasifiers, and the challenges associated with sourcing slags from other pilot-scale gasification operations. Where possible, this review has discussed characteristics of gasification by-products from Australian coal, using the limited number of samples obtained from recent research programs. However, these outcomes cannot cover the range of Australian coals, or the gasification technologies in which these coals may be used. A representative database on coal slag characteristics is needed. The database should include specific feed coal characteristics and the influence of gasifier operating conditions.

The current project will explore the possibility to extend the database to slags from Australian coals by reproducing them under laboratory conditions as similar as possible to industrial conditions. Initially, the validity of this approach will be tested in the laboratory using coals that have previously been tested in a pilot-scale gasifier and for which data is available. If this approach is shown to be valid, it will be a cost-effective way to quickly build up a database of slag characteristics that can be used to assess potential applications.

8.2 Recommendations

To facilitate the uptake of slag by-products, producers and potential end users must be familiar with the characteristics of slags and fly ashes. They must know how these characteristics:

- are affected by feedstock variety
- depend on gasifier types and operational conditions
- satisfy the application requirements.

This knowledge can be obtained by:

- generation of a database related to Australian coal
- extension of the database using modelling tools
- demonstration of particular applications of slag by-products in industry.

Generation of such a database is an expensive, but necessary, step. It will ensure the widespread acceptance of slag as a valuable by-product, rather than it being viewed as waste. Where possible, to the database should use data obtained from pilot-scale gasifiers in which Australian coals have been tested under a range of gasifier operating conditions.

Variation in leaching tests used for environmental assessment of by-products suggests a need for a detailed comparison of leaching test results, and identification of potential uncertainties associated with differences in the test procedures.

Another approach is to obtain data from laboratory samples produced under conditions that reproduce characteristics similar to those of industrial samples. As part of this project, a feasibility study will investigate the viability of this approach.

One outcome of this review is that gasifier slags appear to have characteristics that make them likely candidates for use in the cement industry. Accordingly, preliminary testing of the slag for this application will be undertaken as a part of the laboratory work.

In a consideration of gasifier slag end use, a recommendation from the Australian coal industry suggests that 'a thorough understanding of the logistics and subsequent economic value of the material on a case-by-case basis is necessary before undertaking such an endeavour. However, note that despite the potential lack of viability in some geographical regions, research into the field is strongly advised, as government regulation of waste disposal and carbon taxing are plausible scenarios. These scenarios would act as significant drivers to further development of the ash utilisation industry'.

Part II Laboratory Program

1 Scope of laboratory program

The review of legislation and international use options of gasification by-products in Part I of this report has highlighted a number of issues related to disposal and use of gasification slags. One of these is the lack of an appropriate classification strategy and set of criteria for gasification slags. Notwithstanding this, any new schemes (or application of current schemes designed for wastes from coal combustion) must rely on determination of toxic species present in materials and the extent to which they are able to be mobilised in the environment.

In light of the importance of trace element concentration and behaviour on slag classification and use, this laboratory program aims to study, where possible, the behaviour of trace species in slags obtained from entrained flow gasification of Australian coals. As industrial slag samples are generally uncommon, this program is also investigating the relevance of laboratory-based slag preparation and characterisation techniques to the study of the environmental performance of gasification-derived slags.

The laboratory program of the project has three main components:

- assessing the composition and leaching characteristics of slags in terms of their compliance to existing regulative standards
- evaluating the composition and leaching characteristics of laboratory-made slags, and comparing them with slags made under industrial entrained flow gasification conditions
- obtaining preliminary characterisation of slags for application in the cement industry.

The first aspect of the laboratory program provides some insights into the composition and leaching potential of the trace components in slags obtained from demonstration and pilot-scale gasification facilities. The results are evaluated in terms of the manner in which they would be likely to position the slags in the current regulations across Australian states. Results of the different test procedures and results of the same standard test made in different laboratories are compared to validate their applicability.

The second part of the laboratory program is a feasibility study of the viability of using laboratory-produced slag samples to assess coals in terms of trace element behaviour and leaching characteristics. The approach is to obtain data from laboratory samples produced under conditions that reproduce characteristics similar to those of industrial samples.

The third aspect of the laboratory work analyses the characteristics of gasification slags that are required to assess options for use in the cement industry.

2 Characteristics of slags from entrained flow gasification of Australian coals

2.1 Analytical techniques

Slags produced from the gasification of Australian coals in pilot-scale and larger-scale entrained flow gasifier facilities are available. They offer us the opportunity for characterisation of their trace element concentrations and leachability. These two criteria are the most likely to be important for their classification as wastes (based on the outcomes of Part 1 of this report).

The major element chemical and mineralogical composition of the slags and fine particulates were determined by X-ray fluorescence spectrometry (XRF) and quantitative X-ray diffraction (XRD). The trace elements were determined by either ICP-MS or ICP-AES following acid digestion. Selected samples of the slags were analysed by electron probe microanalysis (EPMA).

To allow a preliminary comparison of slag composition and leaching behaviour with regulations relevant to slag and coal ash disposal and use, ASLP and TCLP tests were conducted on the samples described in Section 2.1 (in Part 1 of this report). These standard tests are widely used in Australia¹ to assess the performance of waste materials against environmental regulations. The ASLP is Australia's version of the TCLP, which includes the two buffering solutions (pH 5.0 and 2.88) used in the TCLP test, as well as reagent, or local water, or tetraborate pH 9.2 (for acid volatile target analytes and in the situation of co-disposal). The maximum sample particle size of samples also differs (2.4 mm for ASLP and 9.5 mm for TCLP).

In the present work, three buffer solutions, neutral (for ASLP requirements only) and pH 2.9 and 5.0 (for both ASLP and TCLP requirements) were used. Water extraction (neutral) with two S/L ratios (3.5 and 20) was used in CSIRO leaching tests.

As discussed in Part 1, the results of leaching tests may vary across different laboratories. Therefore, a series of TCLP and ASLP leaching tests were performed in three independent laboratories:

- Analytical Reference Laboratory Pty. Ltd., ARL (Western Australia), abbreviated as L1
- Australian Laboratory Services Pty. Ltd., ALS (Queensland) abbreviated as L2
- CSIRO/UNSW, abbreviated as L3.

2.2 Slag samples

Slag samples discussed in this section were obtained from three different gasification facilities:

- the Siemens 5 MW pilot-scale gasifier, as part of the CCSD pilot-scale testing program [1, 2]
- two slag samples from two commercial gasifiers.

Some of the characteristics of the slags and fine particulates produced in the Siemens pilot-scale gasifier and IGCC plant have been discussed in Part I of this report. This section provides more detail and compares the results with previously unavailable data on these slags and slags from the commercial gasifiers.

¹ As discussed in the Review, the TCLP is used in ACT, NSW and Queensland regulations, while other states use the ASLP.

This work compares bulk composition and trace element concentrations of raw slag samples from all three gasification facilities, as well as for fine particulates obtained from the Siemens pilot-scale gasifier. Coarse slags in glassy form (frit fractions) were also analysed for phase composition.

The samples are listed in Table 49.

Coal	CRC701	CRC701	CRC702	CRC703	CRC704	S259	ANL001
Raw slag	T100	T101	T102	T103	T104	T105	T106
FRIT	s100	s101	s102	s103	s104	s105	s106
Fine particulates	NA	a101	a102	a103	a104	NA	NA

Table 49: Australian coals and their gasification by-products used as samples for characterisation in this work. NA, samples not available

Figure 2 shows raw slags (as received) and their frit fractions as listed in Table 49.

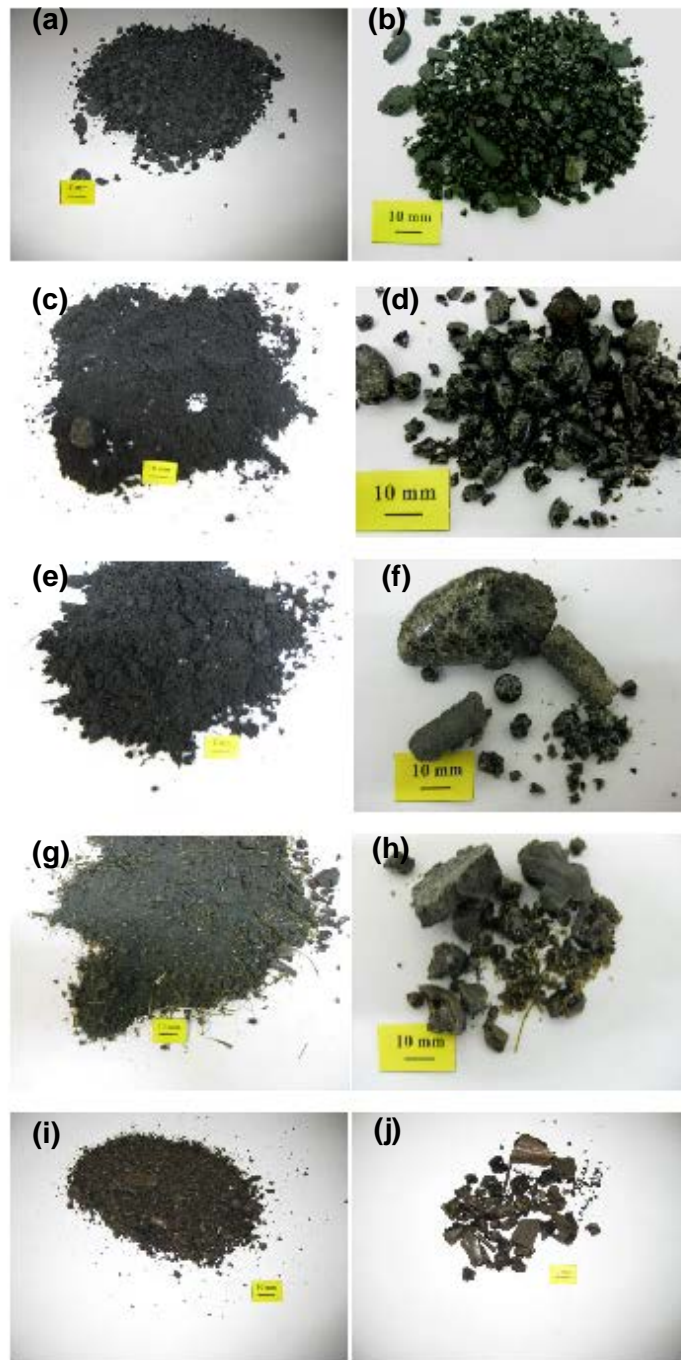


Figure 2. Raw slags (left column) and coarse (frit) slags used in laboratory work: T101(a), s101(b) from CRC701 coal; T102(c), s102(d) from CRC702 coal; T103(e), s103(f) from CRC703f coal; T104(g), s104(h) from CRC701 coal; T106(i), s106(j) from ANL001 coal

The colour, size and morphology of the slags obtained from the pilot-scale tests completed at the Siemens facility in Germany are illustrated in Figure 2. There is a considerable variation in the sizes and morphology of the gasifier slags. This variation is related to factors such as the fusibility of the coal, the composition of the mineral matter and the temperature of gasification. It is likely that variation in the morphology (i.e. particle size and shape, amount of fine material) will affect the leaching characteristics of a particular slag.

2.3 Slag characterisation

Bulk compositions of the raw slags and the composition of coal ashes produced from the same parent coals are listed in Table 50. The major element chemistry of the slags and fine particulates is given in Table 51. Silica, alumina and iron oxide are the dominant components. Calcium is also a significant component in samples T103, T105 and T106. Unburnt carbon content tends to be higher in the fine particulates and is high in all by-products from CRC702 and CRC703 coals. The detailed compositions of slags from the Siemens pilot-scale program, including their microstructure, have been described in previous work [1, 3].

Quantitative XRD analysis reveals that most of the slags were nearly fully molten and the major component is an amorphous phase. There are some crystalline phases, which have two origins: undissolved minerals of the coals such as quartz, and phases crystallised out of slag liquid phase, such as anorthite iron oxides and hercynite. Samples T102 and T103, in particular, have graphitic components; this is annealed, unconverted carbon that is related to the relative conversion performance of these coals. There are no significant differences in the phase composition of the slags and fine particulates.

The presence of relict coal minerals, such as quartz and unburnt carbon, in raw slags suggest either low gasification temperatures or shorter residence times, leading to incomplete gasification. The slag compositions are broadly similar to those of typical pf ashes, although the high iron content of samples T100, T101 and T102 and high calcium content of samples T103, T105 and T106 are significantly higher than those usually found in Australian pf ashes. As a result of the higher iron and calcium contents, silica contents tend to be lower than that of a typical fly ash.

The phases observed in the coarse slag samples (frit fractions) are listed in Table 52, and the microstructures are illustrated in Figure 6 (Section 3.3.2), which supports observations of the raw slags described above. Indices *i* in the samples s100(*i*)–s104(*i*) samples correspond to different ‘steady state’ conditions in the pilot-scale gasifier. The presence of silica or alumina, or alumina with feldspar in the liquid phase of slags s101 and s102, indicates that there was insufficient time for equilibrium to be reached, as these phases cannot be achieved for slags of these compositions at equilibrium. Slag residence time in the pilot-scale gasifier was estimated using available data on the basis of mass balance, slag viscosity, and gasifier geometry. It is estimated that for those for coals used in the pilot plant, the residence time varies from 10 to 30 min, which is likely to be insufficient to fully achieve phase equilibrium in these slags.

The presence of unburnt carbon in slags likely increases the leachability of trace elements from these samples, while the amorphous nature of most of the slags suggests that they have low leaching potential.

Test	CRC701	T100	T101	CRC702	T102	CRC703f	T103	CRC704	T104	S259f	T105	ANL001*	T106
Moisture	6.4	0.3	<0.1	1.3	0.6	0.9	0.6	2.3	<0.1	2.5	<0.1	3.4	<0.1
Ash yield	5.6	99.8	100.4	8.7	89.5	9.6	71.3	11.7	100.0	14	99.8	16.7	96.9
Fixed carbon	51.8	1.1	1.7	55.6	11.7	82.3	21.6	41.9	0.9	49.5	1.4	54.2	3.1
Volatile	36.2			34.4		7.2		44.1		34.0		25.7	
Amorphous phase		85.5	97.9		86.1		74.6		100.0		100.0		95.0
SiO ₂	41.4	41.5	48.2	46.1	41.6	39.5	34.8	47.4	51.1	49.6	54.5	42.2	46.3
Al ₂ O ₃	18.8	21.5	18.9	27.7	21.2	25.6	21.5	33.7	32.1	25.0	22.0	14.6	15.7
CaO	3.41	9.94	4.86	6.6	7.21	15.8	12.8	5.7	7.31	13.2	14.9	11.4	13.5
Fe ₂ O ₃	22.9	21.5	23.2	12.3	13.2	2.2	3.16	4.3	5.84	6.82	6.73	23.3	22.9
MgO	1.99	2.80	2.18	0.5	0.77	1.0	0.93	1.8	2.08	0.55	1.12	1.87	1.77
K ₂ O	0.45	0.48	0.45	0.6	0.22	0.4	0.47	0.7	0.60	0.32	0.78	0.35	0.29
Na ₂ O	0.55	1.51	0.58	<0.1	<0.1	0.7	0.72	0.6	0.96	0.14	0.22	0.35	0.33
P ₂ O ₅	1.37	0.64	0.85	0.1	1.52	1.6	1.21	<0.1	0.14	1.09	0.16	0.52	0.53
SO ₃	5.9	0.60	0.45	1.9	0.43	3.7	0.32	4.2	0.05	1.64	0.22	3.05	1.2
TiO ₂	1.21	0.85	1.13	1.6	1.33	1.2	1.03	1.5	1.68	1.73	1.07	0.72	0.81

Table 50: Characteristics of coal ashes and raw slags studied in this work. *indicative coal ash data

	CRC701		CRC702		CRC703		CRC704	
Sample	s101	a101	s102	a102	s103	a103	s104	a104
wt%								
C	0.25	13.84	9.07	4.54	12.13	20.47	1.18	6.61
SiO ₂	49.39	29.31	41.61	44.72	38.96	38.05	48.33	43.43
Al ₂ O ₃	18.22	19.05	21.25	20.09	24.07	18.74	30.01	22.83
CaO	3.18	2.89	7.34	5.90	14.93	10.36	8.48	6.61
Fe ₂ O ₃	24.79	20.94	13.47	10.29	3.27	2.39	5.87	5.61
MgO	1.76	2.03	0.74	0.51	1.04	0.74	1.91	2.09
K ₂ O	0.43	0.41	0.23	0.26	0.46	0.76	0.54	0.69
Na ₂ O	0.61	0.80	0.27	0.24	0.97	1.16	1.16	1.71
P ₂ O ₅	0.77	2.02	1.56	5.32	1.24	1.93	0.34	0.28
SO ₃	0.38	1.15	0.14	1.05	0.07	0.24	0.10	0.62
TiO ₂	1.20	1.09	1.41	1.61	1.23	0.80	1.63	1.72
MnO	0.09	0.12	0.09	0.09	0.03	0.02	0.04	0.04
LOI	1.57	19.41	10.23	9.32	13.17	24.65	1.18	13.83

Table 51: Major element chemistry of the coarse slags and fine particulates

Coal/ Sample ID	Phase assembly			Estimated tapping temperature, °C
	Major	Minor	Rare	
CRC701 (run1)				
S100(1)	L+A	L+A+F	L+Cr	1340–1450
S100(2)	L+S (+FeS), L	L+A, L+F		1340–1450
S100(3)	L, L+S	L+S (+FeS)	L(por)	>1340
CRC701 (run2)				
S101(1)	L+S	L+S(+FeS)		>1340
S101(2)	L+S	L		>1340
S101(2)	L+S, L		L(por)	>1340
S101(3)	L+S, L			>1340
CRC702				
S102(1)	L+S,			>1360
S102(2)	L+S, L			>1360
S102(3)	L	L+S		>1360
S102(4)	L	L+S		>1360
CRC703				
S103(1)	L+F	L		1380–1480
S103(2)	L+F	L, F+L		1380–1480
S103(3)	F+L	L+F	L+F+S	<1150–1420
S103(4)	F+L	L,L+F,	L(por)	<1150–1420
CRC704				
S104(1)	L+F, L			>1420
S104(2)	L, L+F			>1430
S104(3)	L,L+F	L+F+A		>1430
S104(4)	L, L+F		L+S	>1430

Table 52: Phase appearance in coarse slags and estimated tapping temperatures. L, liquid; L(por), liquid with porosity; A, alumina; S, silica; F, feldspar. Dominant phase in two or three-phase compositions is listed first

2.4 Trace elements in solid residues

Although the abundance of most trace elements in slags is similar to that observed in Australian fly ashes, some differences do exist (Table 53). Of these, the most significant are higher contents of B, Cr, Ni and Sn, and lower concentrations of Zn, Ge, Se and Sb in slags.

In some instances, there is also a significant difference in trace element contents between the slag and corresponding fine particulates (such as ash) from gasification. Chromium contents are lower in three of the fine particulate samples compared with slags from the same coal, and Ga, As, Sb, Pb and Bi are higher in all four particulate samples. Of the other elements, Zn, Ge, Se, and Ti are enriched in three of the fine particulate samples. These enrichments in the fine particulate samples probably represent the greater volatility of these elements and their recapture in fly ash during cooling [7]. The variability in the degree of enrichment may be due to their mode of occurrence in the original coal and the consequent mineralogical changes occurring during gasification.

2.5 Leaching tests

Table 54 and Table 55 show ASLP and TCLP test results, respectively, conducted in laboratories L1 and L2. Bold figures indicate relatively high concentrations (which exceed 1 mg/l). Coloured data represent the data that differ between laboratories by more than 100%. Leaching tests were conducted for all raw slags from the pilot-scale tests and on those from the MHI entrained flow gasifier.

The results of the water and TCLP leach tests conducted in laboratory L3 are given in Table 56 and Table 57, respectively, for the slags and fine particulates. Although gasification slags are generally considered to be relatively inert when compared to pf ashes, it is clear that this is not always the case. For these samples, Al, As, Mo, Co and Si contents in the leachates are comparable to those found for pf fly ashes. However contents of elements such as Mn, Cr, Se, Ni, Cd, and Pb tend to be lower. As might be expected, the fine particulate samples from gasification are more leachable reactive, and many of the elements show a similar behaviour to that found for typical Australian fly ashes.

Concentrations in leachates exceeding 1 mg/l are shown in bold figures in Tables 54–57. Within these elements, only Co, Mn, Ni, Pb (exceeded in fly ash leachates only) and Zn (exceeded in both slag and fly ash leachates) are the elements specified in Australian regulations.

As discussed in the review, raw slag (a mixture of frit and fine particulates, as well as possibly some residual carbon) has relatively higher leachability than coarse slags (frit fraction alone). For disposal purposes, it is unlikely that slag will be present only as a frit fraction. Therefore, raw slag needs to be considered as the most likely material for disposal. Slag beneficiation (i.e. separation of coarse slag material from fine particulates and unburned carbon) may be required if raw slag has trace elements concentration and leaching characteristics that exceed the disposal limits.

Fine particulates in the slag also have high concentration of trace elements, and a greater propensity to leach these species than raw and coarse slags. In this laboratory work, available fly ash samples were also analysed for their compliance to disposal criteria (see Table 59).

Sample	T101	a101	T102	a102	T103	a103	T104	a104	T105	T106
Li	22	19	43	46	186	178	89	58	62	85
Be	19	26	5.8	6.6	3.6	2.7	4.0	7.2	9	3.6
B	38	71	170	200	39	31	77	230	120	80
Sc	17	21	28	26	19	18	29	32	26	21
V	142	152	134	183	124	136	239	291	170	114
Cr	191	141	320	156	228	44.0	198	62	93	99
Co	262	117	557	115	69	59	44	49	51	43
Ni	325	250	692	584	132	76	94	75	76	94
Cu	157	159	469	323	62	29	70	145	29	74
Zn	30	1240	207	292	110	852	42	348	10	20
Ga	179	292	100	263	31	91	61	192	nd	81
Ge	0.7	3.1	1.1	22	0.6	2.9	0.6	6.2	nd	2.4
As	2.8	32	7.1	105	3.3	11	3.1	28	2.7	4.3
Se	0.3	18	4.0	94.0	0.7	4.40	0.3	7.10	nd	0.2
Sr	2530	3160	1690	2240	556	520	1570	1950	530	429
Y	108	126	64	74	47	50	73	90	73	40
Zr	221	152	20	196	17	54.0	799	678	nd	363
Nb	49	48	15	14.5	13	7.89	16	15.7	16	10
Mo	16	60	12	17	5	5.78	8	22	4	3
Ag	3.9	1.51	2.6	2.66	2.3	2.10	4.0	3.70	nd	1.8
Cd	0.45	5.03	0.47	4.01	0.38	1.02	0.50	1.38	nd	0.24
Sn	4	25	24	21	18	1.83	10	22	nd	2
Sb	<0.1	2.93	0.4	2.85	0.2	2.54	<0.1	3.60	0.2	1.3
Te	0.4	3.08	0.1	2.40	0.1	0.79	0.1	0.81	nd	0.1
Cs	2.2	3.02	0.8	1.46	1.7	3.97	2.9	4.65	nd	1.7
Ba	4480	5450	2450	3580	632	439	1480	1680	840	1470
Hf	7	4.11	1	5.48	1	1.37	21	20	nd	8
Ta	2.3	2.58	0.3	0.73	<0.1	0.43	<0.1	0.57	nd	<0.1
W	4	8.10	2	2.68	3	2.52	2	3.56	5	2
Re	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	nd	<0.1
Hg	<0.01	1.10	0.19	4.50	0.10	0.86	0.02	0.92	nd	<0.01
Tl	2.6	39	0.5	5.72	0.2	0.57	0.3	2.42	nd	0.0
Pb	2.8	203	12	174	10	96	6.5	232	nd	2.6
Bi	0.2	6.30	0.6	10	0.4	3.09	0.1	3.49	nd	<0.1
Th	41	38	16	18	15	16	24	23	17	17
U	11	12	4.5	5.73	5.6	7.44	6.9	8.06	6	5.7

Table 53: Trace element chemistry of the slags and fine particulates (mg/kg). nd, not detected

element	Detection Limit		a101		a104		T101		T102		T103		T104		T106	
	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2
Ag	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al	0.1	0.1	0.1	0.9	0.2	<0.1	0.1	0.5	<0.1	0.4	0.7	1.2	0.1	1.5	0.1	0.5
As	0.001	0.01	0.006	<0.01	0.005	<0.01	0.007	<0.01	0.002	<0.01	0.002	<0.01	0.002	<0.01	<0.001	<0.01
Ba	0.01	0.1	0.07	0.10	0.04	0.10	0.02	0.10	0.06	0.20	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1
Be	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B	0.01	0.01	0.29	0.20	0.26	0.20	0.19	0.20	0.22	0.20	0.19	0.20	0.19	0.20	0.18	0.20
Cd	0.002	0.005	0.038	0.034	<0.002	<0.005	<0.002	<0.005	<0.002	<0.005	<0.002	<0.005	<0.002	<0.005	<0.002	<0.005
Co	0.01	0.01	0.12	NA	0.02	NA	<0.01	NA	<0.01	NA	<0.01	NA	<0.01	N/A	<0.01	NA
Cr	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	0.01	0.01	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Hg	0.0002	0.0001	<0.0002	<0.0001	<0.0002	<0.0001	<0.0002	<0.0001	<0.0002	<0.0001	<0.0002	<0.0001	<0.0002	<0.0001	<0.0002	<0.0001
Mn	0.01	0.01	2.5	2.6	0.29	0.26	0.03	<0.01	0.02	0.03	<0.01	0.04	<0.01	0.03	<0.01	0.06
Mo	0.01	0.01	<0.01	<0.01	0.06	0.09	<0.01	<0.01	0.02	0.02	0.02	0.02	<0.01	0.01	<0.01	<0.01
Ni	0.01	0.01	0.40	0.39	0.04	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0.01	0.01	0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01
Se	0.001	0.01	0.009	0.050	0.012	0.020	0.001	<0.01	0.010	0.030	0.004	<0.01	<0.001	0.020	<0.001	<0.01
V	0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01
Zn	0.01	0.01	6.80	8.71	0.59	0.20	0.04	0.03	0.01	0.03	<0.01	0.01	<0.01	0.01	<0.01	0.02

Table 54: ASLP test results (mg/l) for slags and fly ashes from Australian coal gasification. Prefixes L1 and L2 correspond to ARL and ALS laboratory data respectively. Bold figures concentrations exceed 1 mg/l. Coloured data represent the data that differ between laboratories by more than 100%

Element	Detection Limit		a101		a104		T101		T102		T103		T104		T106	
	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2	L1	L2
Ag	0.01	0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1
Al	0.1	0.1	86	5	60	7	28	1	33	1	63	2	37	2	22	<0.1
As	0.001	0.1	0.014	<0.1	0.015	<0.1	0.003	<0.1	0.002	<0.1	0.002	<0.1	<0.001	<0.1	<0.001	<0.1
Ba	0.01	0.1	0.27	0.20	0.64	0.30	1.3	0.3	0.73	0.80	0.57	0.30	0.46	0.50	0.76	0.40
Be	0.01	0.05	0.04	<0.05	<0.01	<0.05	<0.01	<0.05	<0.01	<0.05	<0.01	<0.05	<0.01	<0.05	<0.01	<0.05
B	0.01	0.1	0.38	<0.1	0.33	0.10	0.21	<0.1	0.48	0.20	0.30	<0.1	0.22	<0.1	0.20	0.10
Cd	0.002	0.05	0.087	0.070	0.038	<0.05	0.003	<0.05	0.005	<0.05	0.004	<0.05	<0.002	<0.05	<0.002	<0.05
Co	0.01	NA	0.21	NA	0.12	NA	0.03	NA	0.04	NA	0.08	NA	0.02	NA	<0.01	NA
Cr	0.01	0.1	0.08	<0.1	0.03	<0.1	0.07	<0.1	0.12	<0.1	0.20	<0.1	0.09	<0.1	0.19	<0.1
Cu	0.01	0.1	0.84	0.70	0.15	<0.1	0.07	<0.1	0.20	<0.1	0.14	<0.1	0.06	<0.1	0.03	<0.1
Hg	0.0002	0.001	<0.0002	<0.001	<0.0002	<0.001	<0.0002	<0.001	<0.0002	<0.001	<0.0002	<0.001	<0.0002	<0.001	<0.0002	<0.001
Mn	0.01	0.1	3.6	3.4	1.1	0.8	0.29	<0.1	0.84	0.30	0.43	0.20	0.14	0.20	2.8	0.5
Mo	0.01	0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1	<0.01	<0.1
Ni	0.01	0.01	0.64	0.50	0.30	<0.1	0.14	<0.1	0.92	0.40	0.24	<0.1	0.13	0.20	<0.01	0.30
Pb	0.01	0.01	0.28	0.10	0.32	<0.1	0.08	<0.1	0.16	<0.1	0.29	<0.1	0.10	<0.1	0.16	<0.1
Se	0.001	0.05	<0.001	<0.05	<0.001	<0.05	<0.001	<0.05	<0.001	<0.05	<0.001	<0.05	<0.001	<0.05	<0.001	<0.05
V	0.01	0.1	<0.01	<0.1	0.03	<0.1	0.02	<0.1	<0.01	<0.1	<0.01	<0.1	0.03	<0.1	0.10	<0.1
Zn	0.01	0.1	18	15	21	5	2.6	<0.1	5.4	4.9	2.4	1.2	0.62	0.90	0.37	0.40

Table 55: TCLP test results for slags and fly ashes from Australian coal gasification. Prefixes L1 and L2 correspond to ARL (buffer solution pH 2.9) and ALS (buffer solution pH 5.0) laboratory data respectively. Bold figures concentrations exceed 1 mg/l. Coloured data represent the concentration differences by more than 100%

L/S ratio	T101			T102			T103			T104			T106		
	1:3.5	1:20	TCLP	1:3.5	1:20	TCLP	1:3.5	1:20	TCLP	1:3.5	1:20	TCLP	1:3.5	1:20	TCLP
Concentration in leachates, mg/L															
Al	0.5	0.7	1.5	0.2	0.6	1.3	3.4	3.4	3.1	2.2	2.4	2.3	0.1	0.3	0.4
Ca	11	2.8	4	195	39	99	147	32	155	21	8.0	18	32	6.1	12
Fe	<0.05	<0.05	1.95	<0.05	<0.05	0.03	<0.05	<0.05	0.03	0.08	0.06	0.33	<0.05	0.49	187
K	0.8	0.4	0.2	2.0	0.5	1.8	1.4	5.7	1.2	0.5	0.3	0.4	2.1	0.4	0.5
Mg	2.3	0.6	0.5	9.5	1.8	3.9	3.9	0.9	2.7	2.3	0.6	1.0	1.9	0.6	0.6
Na	2.2	0.5	ND	4.8	1.0	ND	9.8	2.0	ND	7.0	1.5	ND	4.1	0.8	ND
P	<0.2	0.3	<0.5	<0.2	0.4	0.5	<0.2	0.2	<0.5	0.5	0.5	<0.5	2.5	0.5	0.5
S	7.7	1.5	1	183	31	33	120	21	17	17	3.0	3	22	4.2	2
Si	1.9	1.5	2	2.9	1.5	10	0.7	1.4	22	1.2	1.8	4	4.1	2.9	8
Sr	0.45	0.12	0.2	2.3	0.61	1.7	0.4	0.1	0.4	0.3	0.11	0.2	0.06	0.01	0.0
Concentration in leachates, µg/L															
Li	118	26	3	55	11	16	133	28	26	33	22	6	57	23	7
Be	<0.05	<0.05	0.5	<0.05	<0.05	0.6	<0.05	<0.05	0.3	<0.05	<0.05	0.3	<0.05	<0.05	0.2
V	2.6	1.8	0.3	1.7	1.8	2.0	7.8	8.5	3.5	6.6	6.5	0.7	<0.3	<0.3	6.0
Cr	<0.3	<0.3	2	0.8	0.3	<1	1.1	<0.3	1	0.4	0.5	2	<0.3	<0.3	8
Mn	8.8	4.1	64	67.1	9.1	331	1.8	0.3	148	2.2	1.1	95	2.4	3.4	479
Co	0.4	0.1	5	2.4	0.3	16	0.8	0.2	50	0.4	0.1	10	<0.1	0.1	13
Ni	6.7	1.9	49	69	8.2	332	2.5	2.3	58	3.2	1.2	136	1.1	0.5	34
Cu	<1	<1	16	<1	<1	17	<1	<1	25	<1	<1	42	<1	<1	<5

Zn	<1	<1	259	24	<1	3900	<1	<1	1120	<1	<1	448	<1	<1	35
Ga	3.7	1.4	0.2	4.2	4.9	0.1	52	15	0.3	30	8.3	0.3	1.2	2.1	0.2
Ba	92	29	423	126	112	703	23	5	234	28	13	231	7.0	1.6	137
As	0.8	0.6	0.4	3.8	5.1	8.9	2.2	3.0	2.6	3.5	2.6	0.8	<0.3	<0.3	0.8
Rb	1.7	0.5	1.0	2.9	0.8	4.5	2.4	0.7	1.9	1.2	0.6	0.7	6.2	1.2	1.6
Sc	<5	<5	0.4	<5	<5	0.3	<5	<5	0.9	<5	<5	0.4	<5	<5	0.6
Y	<0.2	<0.2	4	<0.2	<0.2	3	<0.2	<0.2	7	<0.2	<0.2	5	<0.2	<0.2	1
B	41	9	<10	248	99	215	76	36	70	62	18	17	78	20	<10
Re	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02
Tl	0.37	0.15	4	0.26	0.08	7	0.09	<0.05	3	0.14	0.05	1	<0.05	<0.05	<0.02
Pb	<0.2	<0.2	5	<0.2	<0.2	1	<0.2	<0.2	4	<0.2	<0.2	3	<0.2	<0.2	<0.1
Bi	<0.05	<0.05	<0.02	<0.05	<0.05	<0.02	<0.05	<0.05	<0.02	<0.05	<0.05	<0.02	<0.05	<0.05	<0.02
Th	<0.05	<0.05	0.16	<0.05	<0.05	0.01	<0.05	<0.05	0.02	<0.05	<0.05	0.05	<0.05	<0.05	0.04
U	<0.05	<0.05	0.4	0.13	<0.05	0.02	1.44	0.09	0.12	0.29	<0.05	0.4	<0.05	<0.05	0.16
Pb	100	95	47	452	394	698	257	207	252	275	378	99	2770	500	570
Ge	0.3	0.2	0.5	1.7	0.9	4.0	0.7	0.7	3.5	0.5	0.4	1.2	1.1	0.7	3.2
Se	2	<1	<0.2	33	16	9.4	13	5	5.1	15	4	1.0	<1	<1	<0.2
Zr	0.5	0.4	<0.2	0.1	<0.1	<0.2	<0.1	<0.1	<0.2	<0.1	0.3	<0.2	<0.1	<0.1	<0.2
Nb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mo	36	7	1.2	77	15	3.2	88	17	6.8	56	9	1.8	11	2	0.4
Ag	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02
Cd	0.2	<0.1	0.6	0.1	<0.1	2.9	<0.1	<0.1	2.0	<0.1	<0.1	0.7	<0.1	<0.1	0.1

Sn	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	0.4	0.4	0.14	0.2	0.3	0.18	<0.2	<0.2	<0.1
Sb	0.8	0.2	0.2	2.8	0.8	0.4	5.5	1.7	2.6	1.9	0.4	0.5	2.0	0.8	1.1
Te	<2	<2	<0.2	<2	<2	<0.2	<2	<2	0.5	<2	<2	<0.2	<2	<2	<0.2
Cs	0.11	0.04	0.2	0.09	0.03	0.5	0.25	0.06	0.2	0.23	0.10	0.2	0.30	0.06	0.1
Hf	0.3	<0.3	<0.1	<0.3	<0.3	<0.1	<0.3	<0.3	<0.1	<0.3	<0.3	<0.1	<0.3	<0.3	<0.1
Ta	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1
W	3.8	1.0	<0.2	1.3	0.7	<0.2	7.4	1.7	<0.2	1.9	0.4	<0.2	5.2	0.9	<0.2
Ti	0.8	1.3	6	1.0	0.9	2	0.8	0.3	4	1.0	3.7	4	3.7	2.5	3
Hg	0.020	0.005	<0.03	0.007	0.004	<0.03	0.035	0.007	<0.03	0.010	<0.003	<0.03	0.027	<0.003	<0.03

Table 56: Element concentrations in the leachates of slags. Bold figure concentrations exceed 1 mg/l

Fine particulates	a101			a102			a103			a104		
	1 : 3.5	1 : 20	TCLP	1 : 3.5	1 : 20	TCLP	1 : 3.5	1 : 20	TCLP	1 : 3.5	1 : 20	TCLP
Concentration in leachate, mg/L												
Al	0.5	0.2	7.9	0.7	1.4	14	5.9	2.5	10	12.4	5.5	17
B	0.55	0.18	0.16	0.34	0.12	0.17	0.38	0.12	<0.1	0.67	0.16	0.24
Ca	552	117	128	172	50	254	315	59	57	160	38	132
Co	0.51	0.11	0.10	0.01	0.001	0.07	2.72	0.50	0.40	0.22	0.04	0.05
Fe	0.05	<0.05	0.22	0.07	<0.05	0.09	0.24	0.15	0.31	0.06	<0.05	0.07
K	13.2	3.3	9.5	3.7	1.0	5.4	10.7	2.7	5.5	9.9	3.2	8.5
Mg	152.6	27.8	29	6.3	1.5	6.6	104.9	19.0	17	13.2	2.6	4.6
Mn	7.04	1.36	1.38	0.11	0.02	0.67	18.4	3.74	3.14	3.13	0.57	1.03
Na	149.8	29.1	ND	30.7	6.2	ND	81.1	15.4	ND	15.0	3.1	ND
Ni	0.3	<0.1	0.02	<0.1	<0.1	0.12	3.2	0.6	0.49	7.9	1.5	1.73
P	<0.2	<0.2	<0.5	3.6	1.4	2.5	<0.2	<0.2	<0.5	0.5	1.0	5.4
S	972	196	182	145	28	25	587	118	118	208	38	35
Si	16.9	9.8	9	1.6	1.2	46	23.6	10.2	5	23.7	6.8	21
Sr	6.66	2.2	2.8	0.7	0.2	0.9	7.8	3.74	4.4	2.76	1.04	3.4
Zn	11.9	2.9	4.7	0.07	0.01	20	74.6	16.2	14	1.17	0.21	1.8
Concentration in leachate, µg/L												
Li	515	110	126	141	37	62	226	60	38	115	31	28
Be	0.22	0.08	2.5	<0.05	<0.05	0.7	3.81	1.90	7.6	1.49	0.63	1.5
V	<0.3	<0.3	0.3	4.8	7.2	14.5	<0.3	<0.3	0.1	6.2	7.1	22
Cr	<0.3	<0.3	3	0.6	0.5	<1	0.4	0.7	7	<0.3	<0.3	<1

Cu	36	11	303	2	<1	31	434	157	932	9	2	409
Ga	0.8	0.4	2.2	485	349	1.6	4.0	1.3	3.5	2.7	3.3	0.5
Ba	35	58	130	52	15	184	43	62	119	203	105	423
As	0.8	<0.3	1.3	7.5	8.3	6.9	1.8	0.3	1.9	75	56	273
Rb	31	8.8	18	4.0	1.2	4.6	50	13	19	6.3	1.7	3.8
Sc	<5	<5	5.9	<5	<5	2.2	<5	<5	1.8	<5	<5	0.9
Y	15.4	2.4	33	<0.2	<0.2	11	129	34	53	<0.2	<0.2	2
Re	0.1	<0.1	0.10	2.2	0.4	0.35	0.6	0.3	0.26	3.1	0.7	0.5
Tl	7.30	2.13	6	0.10	<0.05	2	339	111	220	4.24	1.38	5
Pb	3.7	1.1	112	<0.2	<0.2	28	8.2	3.0	110	<0.2	<0.2	4
Bi	<0.05	<0.05	0.07	<0.05	<0.05	0.06	<0.05	<0.05	<0.02	<0.05	<0.05	0.06
Th	<0.05	<0.05	0.11	<0.05	<0.05	0.02	<0.05	<0.05	0.14	<0.05	<0.05	0.01
U	<0.05	<0.05	4.2	0.14	<0.05	0.9	0.35	0.08	5.7	<0.05	<0.05	0.2
Pb	<5	<5	<10	2910	1250	391	<5	<5	<10	788	975	6250
Ge	4.7	3.1	4.4	6.3	4.9	35	3.0	1.5	2.2	436	144	118
Se	46	9	11	46	19	9	88	18	17	729	183	116
Zr	<0.1	<0.1	<0.2	0.5	<0.1	<0.2	<0.1	<0.1	<0.2	<0.1	<0.1	<0.2
Nb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mo	10	4	1.7	326	67	48	4	1	1.3	370	119	72
Ag	<0.1	<0.1	0.20	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02	<0.1	<0.1	<0.02
Cd	29	7.2	14	0.75	0.13	17	293	67	71	38	7.1	45
Sn	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	<0.2	1.4	<0.1	<0.2	<0.2	<0.1
Sb	1.3	0.7	1.0	34	11.1	17.1	0.2	0.1	0.4	37	14.5	9.4
Te	<2	<2	0.2	<2	<2	1.1	<2	<2	0.3	<2	<2	1.7

Cs	1.36	0.37	1.2	0.45	0.13	0.8	3.82	1.10	2.4	1.25	0.38	1.1
Hf	<0.3	<0.3	<0.1	0.3	<0.3	<0.1	<0.3	<0.3	<0.1	<0.3	<0.3	<0.1
Ta	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1	<0.2	<0.2	<0.1
W	<0.2	<0.2	<0.2	16.3	4.8	0.9	<0.2	<0.2	<0.2	2.6	2.5	0.4
Ti	3.6	2.2	5	4.9	2.1	5	3.8	1.6	3	3.8	2.3	10
Hg	0.477	0.066	<0.03	0.096	0.025	0.09	0.029	<0.003	<0.03	1.05	0.27	0.04

Table 57: Element concentrations in the leachates of the fine particulates. Bold figures concentrations exceed 1 mg/l. ND, not determined

2.5.1 DIFFERENCES BETWEEN LEACHING TESTS

The main difference between the leaching tests used is in the pH of the buffer solution and the maximum particle size. Leaching results (Table 58) indicate that leaching of each element from the analysed solids is strongly dependent on pH of the buffer solutions. No leaching of Ag, Be, and Hg was observed in both solutions. Pb, Co and Cu are only leachable in both acidic solutions (illustrated for Co in Figure 3a), Cr and V are leachable in pH 2.9 solution only, while Mo (Figure 3b) and Se are leachable in water only. Significantly higher leaching of Al, Ba and Zn (from slag only) is observed in acidic solution.

All slags have leaching characteristics below the lowest ASLP/TCLP limits when reagent water is used as a leachate. If extraction solutions of pH 2.9 and pH 5.0 are used, leaching of Ni exceeds the lowest ASLP/TCLP limit.

In fly ashes, concentrations of lead and nickel are higher than the lowest ASLP/TCLP limits for both extraction methods.

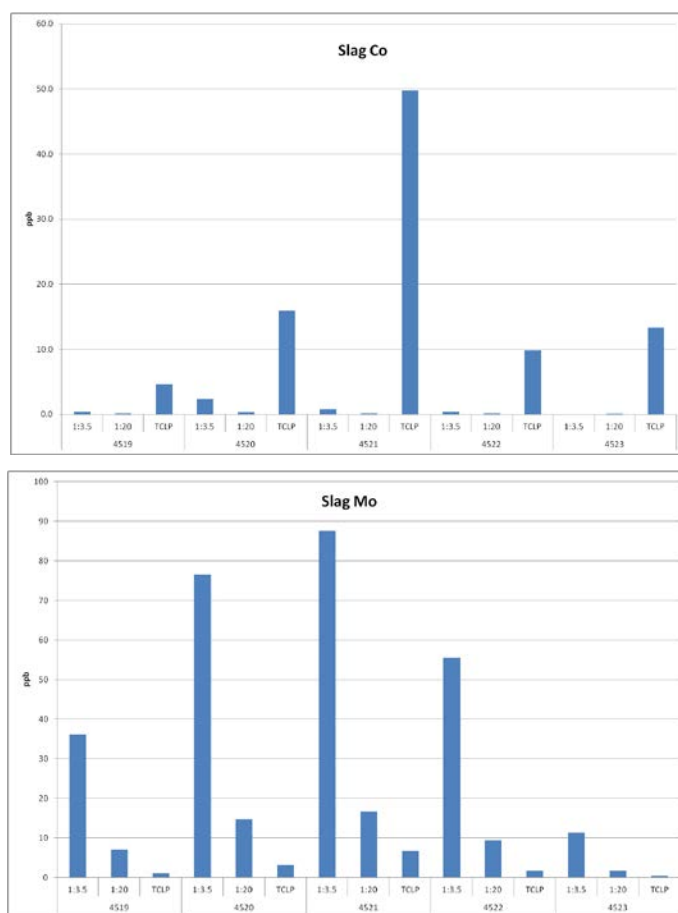


Figure 3. Cobalt leach data (top) shows the typical aggressive behaviour of the TCLP leach, whereas molybdenum leach data (bottom) illustrates the strong pH control on such elements

2.5.2 DIFFERENCES BETWEEN LABORATORIES

Results of ASLP tests from two laboratories (L1 and L2) are comparable for most of the elements. Only Al, Ba, Mn, Se and Zn demonstrate significant variation between laboratories. Aluminium is a major component of slag, and Ba and Mn are significantly higher than other trace elements. Their relative concentrations (% of metals leached from the slag) in leachates are very small, and this is probably the reason for the variation in absolute leaching values. Concentration of Zn and Se is also very low (near the detection limit) in the slag leachates; the error in the measurements is consequently high.

Similar results are observed with TCLP leachates, where significant variations are observed in concentrations of Al, Ba, Mn and Zn. Large variations in concentrations of B, Ni and Pb are also observed; the source of this variation is unclear.

2.5.3 IMPLICATIONS FOR SLAG ENVIRONMENTAL ASSESSMENT

A summary of these results is given in Table 58. The data are compared with RCRA limits as well as ASLP/TCLP limits used in various Australian state regulations. Since the classifications in the states are different and used different ASLP/TCLP limit values, only the lowest and highest limits are presented in the table. All leaching data are well below RCRA limits, as well as below the maximum ASLP/TCLP limits. Only nickel and lead in slags and fly ashes, and selenium in fly ashes, exceed some of the lowest limits.

	Reagent water extraction		pH 2.9 and 5.0 extraction		ASLP/TCLP limits		RCRA limit
	Fly ash	Slag	Fly ash	Slag	Min	Max	
Ag	<0.01	<0.01	<0.01–0.2	<0.01	0.5	100	
Al	0.1–5.5	<0.1–3.4	8–86	22–63	–	–	
As	0.005–0.056	<0.001–0.007	0.001–0.27	<0.001–0.009	0.35	50	5
Ba	0.02–0.1	<0.01–0.112	0.12–0.64	0.046–1.3	35	100	100
Be	<0.01–0.02	<0.01	<0.01–0.04	<0.01	0.1	10	
B	0.12–0.29	0.01–0.22	0.01–0.38	0.01–0.48	15	120	
Cd	<0.002–0.067	<0.002	0.014–0.087	<0.002–0.005	0.1	10	1
Co	0.02–0.5	<0.01	0.05–0.21	<0.01–0.08	–	–	
Cr	<0.01	<0.01	<0.01–0.08	<0.01–0.2	0.5	50	5
Cu	<0.01–0.16	<0.01	0.03–0.93	<0.01–0.2	10	800	
Hg	<0.0003	<0.0002	<0.0002	<0.0002	0.02	1.0	0.2
Mn	0.02–3.7	<0.01–0.03	0.67–3.6	0.06–2.8	50	50	
Mo	<0.01–0.12	<0.01–0.02	<0.01–0.07	<0.01	0.5	50	
Ni	0.04–1.5	<0.01–0.01	0.02–0.64	<0.01–0.92	0.2	8	
Pb	0.01–1.25	<0.01–0.39	<0.01–6.3	0.08–0.70	0.2	20	5
Se	0.009–0.183	<0.001–0.016	<0.001–0.12	<0.001–0.01	0.1	50	1
V	<0.01	<0.01	<0.01–0.03	<0.01–0.1	–	–	
Zn	0.21–16.2	<0.01–0.04	1.8–21	0.04–5.4	150	1,200	

Table 58: ASLP/TCLP leaching test results (mg/l) for Australian coal gasification fly ashes and slags. Shaded data exceed corresponded shaded colour limit. ‘–’, unavailable data

These TCLP/ASLP leaching test results, as well as trace elements concentrations listed in Table 53, were compared with the classification guidelines used in Australian state regulations (Table 59).

The demonstrated differences in leaching test results indicate that leaching characteristics may significantly affect classification of by-products if the total concentration of the elements is significant.

By-product	New South Wales	Australian Capital Territory	Queensland	Victoria	Western Australia	South Australia
Raw slag						
T101	General solid	Inert	General	Industrial	Class iv	Low level contaminated
T102	General solid	Inert	General	Industrial	Class iv	Low level contaminated
T103	General solid	Solid	General	Industrial	Class iv	Intermediate
T104	General solid	Inert	General	Industrial	Class iv	Intermediate
T105	General solid	Inert	General	Industrial	Class iv	Intermediate
T106	General solid	Inert	General	Industrial	Class iv	Intermediate
Fly ash						
a101	General solid	Solid	Limited regulated	Category b	Class iv	Intermediate
a102	Restricted solid	Industrial	Regulated	Category b	Class iv	Intermediate
a103	General solid	Solid	General	Industrial	Class iv	Intermediate
a104	General solid	Solid	General	Category c	Class iv	Intermediate

Table 59: Classification of slags and fly ashes from gasification of Australian coals in Australian State regulations

Table 59 demonstrates that most gasification by-products have the lowest ranking in the classification schemes of all states, in terms the trace elements contamination and their leaching potential, except for Western Australia. Details of the by-product classification in Australian state regulations are given below:

New South Wales: all by-products are ‘general waste’ (the lowest contamination ranking), except for a102 (classed as a ‘restricted solid’) due to its high Se concentration.

Australian Capital Territory: All slags are ‘inert waste’ (lowest contamination ranking), except T103 (‘solid waste’) due to its Ni leaching result being above the lowest limit. Fly ashes a101 and a103 fly are also classified as ‘solid waste’ due to their Ni leaching data; a104 is also ‘solid waste’ due to Ni and Se leaching being above the lowest limit. Without authorised approval of immobilisation, a102 fly ash would probably be classified as ‘industrial’, due to its high Se concentration.

Victoria: All slags and one (a103) fly ash fulfil the criteria for classification as ‘industrial waste’, the lowest contamination ranking. Fly ash a104 would probably be classed as ‘category C’ (due to its Ni leaching being above the lowest limit). Fly ashes a101 and a102 are ‘category B’ (due to high Ba and Se concentrations).

Queensland: All slags, and a103 and a104 fly ashes, are likely to be classified as ‘general waste’, the lowest contamination ranking. Fly ash a101 would probably be classified ‘limited regulated’ waste as its Co concentration exceeds the lowest limit, and a102 as a ‘regulated waste’ due to its high Se concentration.

Western Australia: All by-products are classified as 'Class 4 (secure)', because their total Al and Mg content exceed 20%.

This summary indicates that the status of gasification by-products in the various States waste classification systems tends to be mainly affected by the total concentration of trace elements in their bulk composition, while for some by-products assessed in the Australian Capital Territory and Victoria regulations, the leaching characteristics become more important.

An interesting example of this is the classification of a102 and a104 fly ashes according to the Australian Capital Territory regulations. Concentration of Se in a104 fly ash is relatively low (2.7 mg/kg); however, the concentration of Se in the leachate (1.73 mg/L) exceeds the lowest limit (1 mg/L), which moves a104 into the category of 'solid waste'. Contrary to this, a102 has Se concentration in leachate (0.3 mg/L) well below the lowest limit. However, the total concentration of Se in a102 is high (92.1 mg/L), and this exceeds the limits applied for both 'inert' and 'solid' wastes. Despite the fact that a102 has very low leaching potential (low absolute concentration of Se in leachate and very low relative leachability [% of Se leached from flyash]), this product is classified as 'industrial waste', which is more restrictive than 'solid waste'.

2.6 Summary: Slag compositions and leachability

This section has analysed some slags made from pilot and demonstration-scale entrained flow gasification facilities in terms of their bulk composition, their concentration of trace elements, and the leaching behaviour of these elements in the context of environmental regulations used to assess coal-derived combustion products. Results indicate that these gasification slags and fly ashes are generally low-leaching materials as assessed by common regulative leaching tests (ASLP and TCLP), with the possible exception of Ni and Se. Their classification in Australian regulations, however, is likely to be more affected by their total concentration of trace elements, which may exceed the lower limits for Ba, Co, Se, and Ni, particularly in fly ashes.

One of the limitations of the existing state regulations, therefore, is the manner in which trace element concentrations and their leachability are used in by-product classification. The structure of the assessment process seems to imply that leachability depends on (or is proportional to) the concentration of trace elements in solid residues, which is clearly not always the case.

The influence of feed coal characteristics and gasifier operation on leaching behaviour of the slag is largely unknown and needs to be determined to ensure that the appropriate environmental and legislative requirements can be met. Acknowledgement of the role of waste properties, rather than the origin of the waste, is essential for proper positioning of gasification by-products in Australian regulations.

It is also apparent that classification and disposal practices for gasification solids are dependent on the pH of the buffer solutions used in the leaching test. Unfortunately, not all state regulations provide clear direction regarding the test conditions. They often generally refer to the TCLP test or ASLP test, which offers some degree of flexibility in the choice of buffer solution. It is also important to consider not only the characteristics of the waste material, but also the environment into which it will be disposed, or of the potential end use. Therefore, further research is required to determine the most appropriate leaching test procedures for specific disposal or use scheme.

3 Characteristics of slags prepared in the laboratory

3.1 Introduction

Section 2 demonstrated the importance of access to real slags produced from Australian coals, under realistic entrained flow gasification conditions, to assess their suitability for a range of disposal or use options. Such slag samples are rare and difficult to obtain for characterisation of a specific feedstock or blend. This section explores the possibility of producing slags under laboratory conditions to create samples that can be used to assess the environmental performance of coal sample solid by-products.

This approach will be tested by producing slags in the laboratory from coals that have previously been tested in a pilot-scale gasifier and for which data is available. This is a similar approach to that used to assess flow characteristics of slags, whereby the experimental viscosity data obtained on laboratory slags have a higher degree of the confidence than predicted viscosity data based on coal analyses. However, there are still differences between laboratory and industrial slag composition caused by partitioning of major elements in solid by-products and interaction with wall slag. This leads to the differences between viscosity of laboratory and industrial slags, which can be estimated and taken into account.

3.2 Experimental techniques

Laboratory slags were produced using techniques consistent with those previously used to assess coal slag viscosity behaviour [3, 4]. CRC701 and CRC704 coals were used in this work (see Table 50 for details). A sample of each coal was ashed in a muffle furnace in air at 800 °C. The mixture was then homogenised with a ring mill and pelletised. Samples were then melted in graphite crucibles under a nitrogen atmosphere at 1500–1550 °C in a vertical tube furnace. After 1 h of melting, slag samples were extracted from the crucible by cold-rod quenching. This involves dipping an alumina rod in the molten slag, removing it and then cooling it in water.

The partial pressure of oxygen, pO_2 , in the system was minimised through nitrogen purging through the furnace tube and the use of a graphite crucible lining. pO_2 near the slag can be influenced by nitrogen flow rate and was measured using an oxygen probe. At temperatures of 1200–1600 °C, pO_2 values near the slag surface were detected over 10^{-12} – 10^{-8} atm (Figure 4), which is similar to partial oxygen pressure at the outlet of an entrained flow gasifier [5].

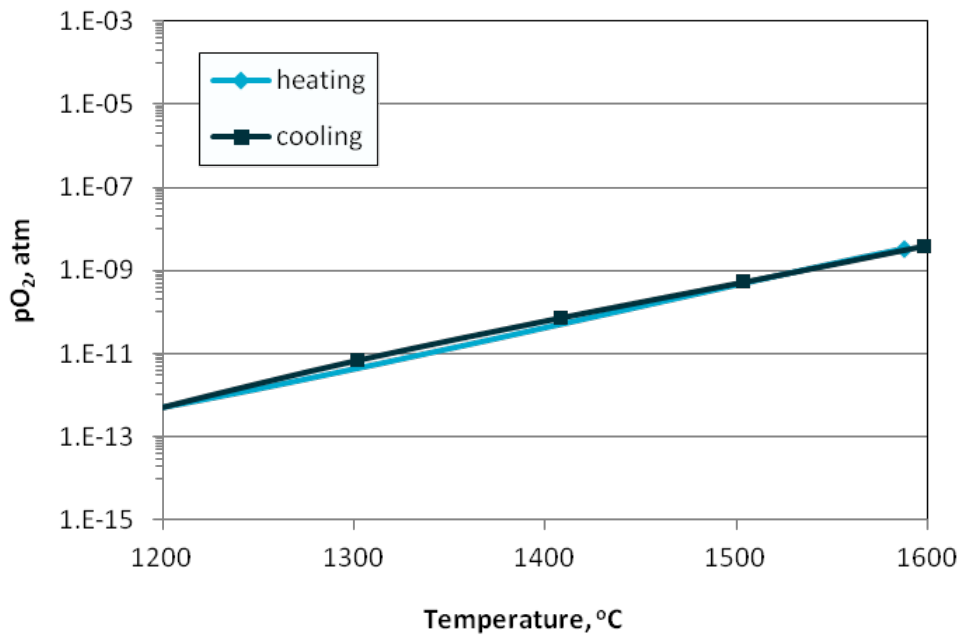


Figure 4. Partial oxygen pressure in laboratory conditions used for slag preparation

The relevant preparation conditions for laboratory and pilot-scale slag formation are listed in Table 60. The major differences in the conditions for slag preparation are total pressure in the system, the gaseous atmospheres present, and the residence time of the slag. FactSage equilibrium calculations on trace elements indicate that total pressure may have some impact on their phase equilibria, while gas composition is only likely to affect the appearance of volatile species, and not those in a condensed form (i.e. slag). Solubility of trace elements in the slags is likely to be determined by slag bulk composition, temperature and partial oxygen pressure, which are similar under laboratory and pilot-scale conditions.

Slag in an entrained flow gasifier is formed in a dynamic (flow-moving) system, while under laboratory conditions, slags are prepared in a static system. Reactions between solid and liquid phases are expected to be faster in dynamic systems. Slag formation time under laboratory conditions is therefore selected to be longer than the calculated slag residence time in a gasifier. As phase equilibrium is often not achieved in a gasifier, however, this time does not have to be sufficient to reach phase equilibrium.

Slag	Temperature, °C	Pressure, atm	Atmosphere	p_{O_2} , atm	Residence time, min	Quenching
Laboratory	1500–1550	1	N ₂ *	$\sim 10^{-9}$	60	Yes
Pilot-scale	1400–1650	25	Variable	10^{-8} - 10^{-12}	10-30	Yes

Table 60: Preparation conditions of laboratory-made and pilot-scale gasifier slag. *Contains trace amounts of CO and CO₂ as a result of graphite reaction with residual O₂

Slag samples produced and used in this study are listed in Table 61.

Coal	Industrial Slag ID	Industrial slag source	Lab Slag ID	Lab slag source
CRC701	s101	Siemens	L101	Lab ashing and melting
CRC704	s104	Siemens	L104	Lab ashing and melting
			Ls104	Remelting of s104
ANL001	T106	Commercial gasifier	LT106	Remelting of T106

Table 61: Laboratory and industrial slag samples used in this study

Industrial slag samples are used as reference samples. Two laboratory samples (Ls104 and LT106) were prepared by-remelting industrial samples to evaluate any effects of conditions in the tube furnace on the conservation of trace elements in the slags. Another two laboratory samples (L101 and L104) were prepared to evaluate trace elements appearance in laboratory slags made from coal ashes.

3.3 Results

3.3.1 SLAG APPEARANCE AND MORPHOLOGY

Laboratory and pilot-scale slags are shown in Figure 5. Laboratory slags form vitreous pieces very similar to the glassy, frit fraction of industrial slags. The portion of slag attached to the cold rod was defragmented into smaller (1–10 mm) pieces during quenching. Some laboratory slags have needle-like fragments (caused by slag flowing during the quenching) similar to the needles observed in pilot-scale slags (Figure 2).

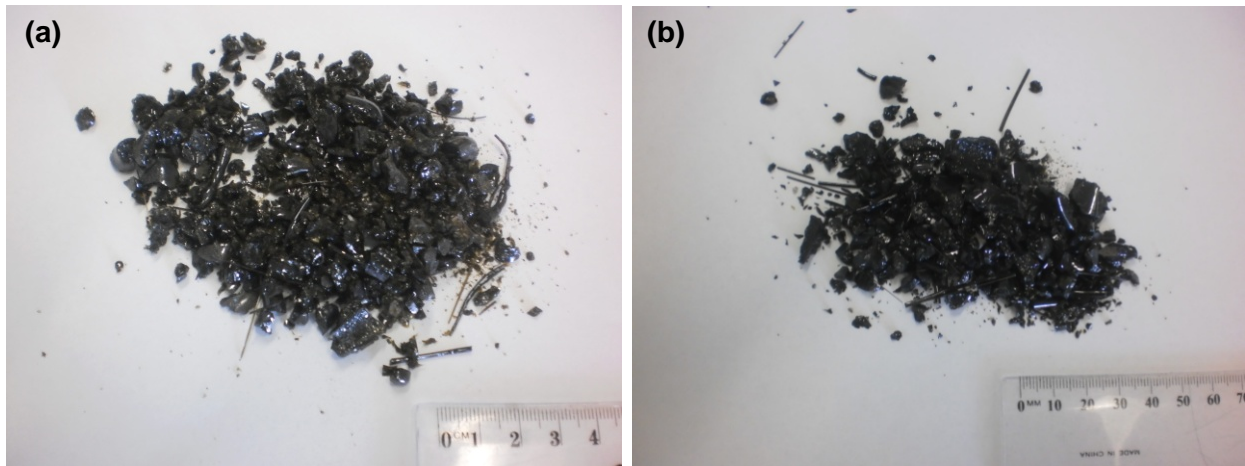


Figure 5: Samples of laboratory slags L701 (a) and L704 (b), obtained from CRC701 and CRC704 coal ashes

3.3.2 SLAG COMPOSITION AND MICROSTRUCTURE

Compositions of coal ashes (major elements) and the corresponding laboratory and pilot-scale slags are listed in Table 62. Phase composition of laboratory and trial slags are shown in Figure 6. The bulk and phase compositions of laboratory and trial slags are very similar.

Parent coal	CRC701			CRC704		
Sample	Ash	L101	s101	Ash	L104	s104
SiO ₂	41.4	46.68	50.1	47.4	50.29	48.3
Al ₂ O ₃	18.8	20.17	18.4	33.7	26.61	29.4
Fe ₂ O ₃	22.9	21.83	24.6	4.3	7.53	5.9
CaO	3.41	3.59	3.3	5.7	6.89	10.4
MgO	1.99	2.23	1.64	1.8	1.99	1.56
P ₂ O ₅	1.37	1.48	0.74	0.1	0.28	0.58
Na ₂ O	0.55	0.67	0.56	0.6	1.07	1.07
K ₂ O	0.45	0.52	0.45	0.7	0.61	0.54
SO ₃	5.9	0.04	0.36	4.2	0.11	0.06
TiO ₂	1.21	1.19	1.18	1.5	1.59	1.56

Table 62: Composition of coal ashes, laboratory and pilot-scale slags

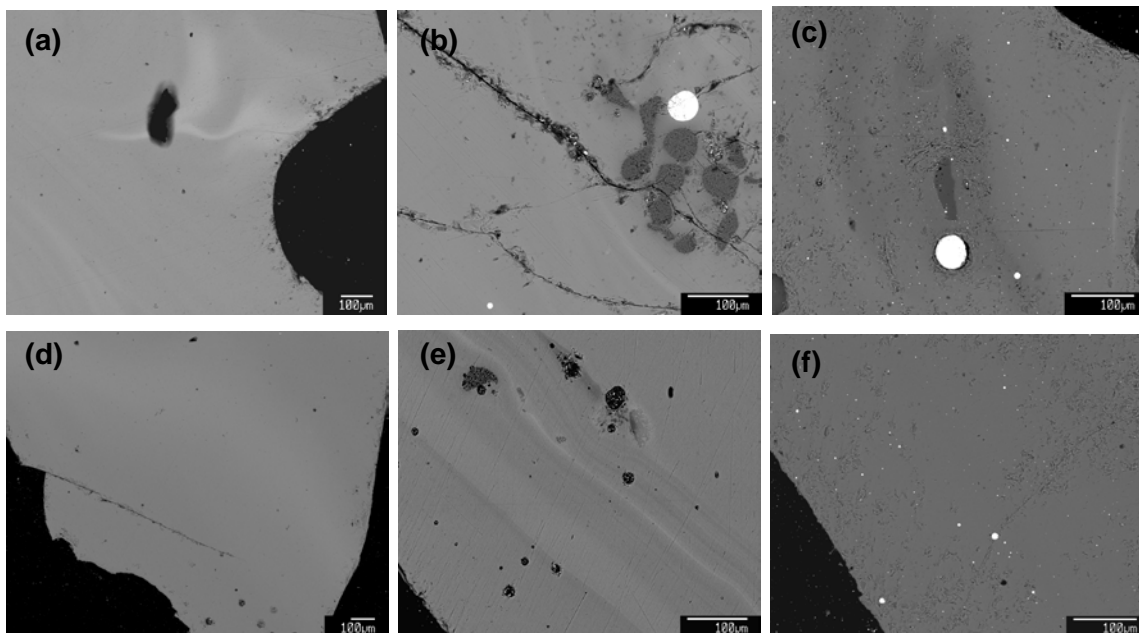


Figure 6. Microstructure of pilot-scale (a, b, d, e) and laboratory slags (c, f) from CRC701 (a-c) and CRC704 (d-f) coals

Both laboratory and pilot-scale slags are mainly amorphous (glass-like) materials with small inclusions of unprocessed² minerals (which appear as dark features) and precipitated metallic iron (white particles). This provides the confidence that the trace elements in laboratory slags are in the same form as in the pilot-scale slags (dissolved in the slag amorphous phase). Precipitation of iron in pilot-scale samples was observed for high iron slags only (i.e. CRC701 coal), while both laboratory slags (from CRC701 and CRC704 coal ashes) contain precipitated iron. This indicates that either more reducing conditions were applied in laboratory slag preparation than in the pilot-scale gasifier, or laboratory slags had a longer residence time than pilot-scale slags. To ensure appropriate use of laboratory slags to assess trace element behaviour under a wide range of gasification conditions and for a wide range of coal samples, more work is required to investigate the separate effects of residence time and gas compositions on the phase compositions of laboratory slags.

3.3.3 TRACE ELEMENTS

Table 63, Table 64 and Table 65 give the concentrations of trace elements in coal ashes, pilot-scale slags, pilot-scale slags after remelting under laboratory conditions, and laboratory-made slags.

The results for solids derived from CRC701 and CRC704 coals are very consistent:

- Concentration of some trace elements in pilot-scale slags is affected by slag on the wall of the gasifier. This is expected to be the cause of pilot-scale slags being enriched in Cr, and possibly Ni as previously reported [6, 7].
- Concentrations of most elements in remelted pilot-scale slags are not lower than in the original pilot-scale slags. This suggests that laboratory slag preparation conditions are not likely to significantly affect concentrations of trace elements, except perhaps Ni. Reduced Ni concentrations in remelted pilot-scale slags and laboratory slags are likely to be due to the dissolution of Ni in precipitated metallic iron, which is not present in pilot-scale slag.
- Laboratory slags are enriched with Co, W and possibly V by graphite crucible contamination (introduced during graphite rod processing). This is an important outcome of this work, and an

² In this context, an 'unprocessed mineral' is one that has not melted to form a slag during the gasification or slag preparation process.

issue that is readily overcome by modification of the procedure for laboratory slag preparation for environmental assessment.

- The volatile elements Bi, Cl, Hg, Zn, Se and Sb are highly volatile in both laboratory and trial slags.
- Arsenic is less volatile in both laboratory slags, while F and Pb are less volatile in laboratory slag L104 only; their volatility most likely depends on residence time, temperature, and oxidation state of other metals in the slags.
- Boron is volatile in pilot-scale samples, but not in laboratory slags. The reason for this is not clear, but may be due to boron capture by wall slag in the gasifier. More work is required to clarify this behaviour.

For the 28 elements examined in laboratory and pilot-scale slags with the techniques described here, 18 have similar concentrations in both samples, 3 show the same trends but experience different degrees of volatilisation, and 7 have different concentrations. The results indicate that laboratory slags made using the techniques used in this work can be used to evaluate trace element concentrations for selective elements only.

For the 16 elements specified in Australian state regulations, 10 can be evaluated using laboratory-made slags. These elements include those that are:

- highly volatile from the slags such as Bi, Hg, Sb, Se: and with certain considerations, As, F and Pb
- expected to remain in the slag: Ba, Cu and possibly Cr (enrichment by refractory or wall slag may complicate the analysis).

Elements that cannot be evaluated using this laboratory slag procedure include:

- boron: may be reactive with gasifier wall slag or become volatile at high pressures
- nickel: slags show some degree of enrichment with Ni from existing gasifier wall slags, and Ni is partially lost under these laboratory conditions due to dissolution in precipitated iron. Less reducing conditions are required to conserve Ni concentration in laboratory slag
- cobalt: trace cobalt in graphite crucible was dissolved in the laboratory slag
- molybdenum: contamination from furnace tube set-up.

The laboratory procedure used in this work to generate slags is suitable for a large number of trace elements of interest to waste classification and use. Importantly, this work has identified some aspects of the technique that require modification to ensure accurate representation of all elements of interest in the slags. These modifications are based on choosing materials for construction of crucibles and quenching rods that do not contaminate the samples. Further work is required to develop a procedure for generating slags in the laboratory that accurately represent industrial slags in terms of trace element concentrations.

Section 3.3.4 addresses the leachability of the trace elements from the laboratory slags.

	T106	LT106	Comments	Used in regulations
As	1.3	nd		Y
B	100	79.6		Y
Ba	1700	1700		Y
Be	4.0	5		Y
Bi	nd	nd		N
Cd	nd	nd		Y
Co	130	240	Enriched by crucible	Y
Cr	93	85		Y
Cu	68	22	Reduced in lab slag	Y
F	80	60		Y
Hg	nd	nd		Y
Li	77	99		N
Mn	3500	4000		Y
Mo	5	820	Enriched by tube furnace contamination	Y
Ni	80	29	Reduced in lab slag	Y
Pb	1.7	0.29	Reduced in lab slag	Y
Sb	1.4	nd		Y
Sc	17	22		N
Se	1.3	0.6		Y
Sn	7	nd	Reduced in lab slag	N
Sr	370	440		N
Th	15.2	18		N
U	4.5	5.4		N
V	100	130		N
W	500	1600	Enriched by crucible	N
Y	38	43		N
Zn	6	12		Y

Table 63: Concentration of trace elements in industrial slag T106 and the slag after remelting (LT106), mg/kg. Bold figures indicate enrichment; figures in blue indicate losses; nd, not detected

	Coal ash	s101	L101	Comments	Used in regulations
As	12.6	0.0	2.3		Y
B	103	1.2	100.0	Volatile from pilot-scale slags only	Y
Ba	4500.0	4600.0	6200.0		Y
Be	18.9	18.0	29.0		Y
Bi	2.2	nd	nd		N
Cd	1.5	0.6	nd		Y
Co	86.0	101.0	430.0	Enriched by crucible	Y
Cr	103.0	197.0	140.0	Enriched by wall slag	Y
Cu	86.0	52.0	54.0		Y
F	690.0	nd	nd		Y
Hg	0.9	nd	nd		Y
Li	17.2	20.0	28.0		N
Mn	600.0	610.0	930.0		Y
Mo	24.0	19.0	54.0	Enriched by tube furnace contamination	Y
Ni	189.0	244.0	72.0	Enriched by wall slag, reduced in lab slag	Y
Pb	55.0	1.5	1.8		Y
Sb	0.9	0.03	nd		Y
Sc	34.0	45.0	23.0		N
Se	14.0	0.3	nd		Y
Sn	6.9	0.6	2.0		N
Sr	2400.0	2400.0	3500.0		N
Th	34.0	42.0	50.0		N
U	8.6	9.7	12.7		N
V	103.0	123.0	230.0	Enriched by crucible?	N
W	3.4	3.6	3100.0	Enriched by crucible	N
Y	93.0	99.0	130.0		N
Zn	413.0	19.0	8.0		Y

Table 64: Concentration of trace elements in CRC701 coal ash and the corresponding pilot-scale and laboratory-prepared slags, mg/kg. Bold figures indicate enrichment; figures in blue indicate losses; nd, not detected

	Coal ash	s104	Ls104	L104	Comments	Used in regulations
As	25.4	0.7	0.4	4.5	Less volatile in lab slag	Y
B	222	2.2	87.8	200.0	Volatile in pilot-scale slag only	Y
Ba	1300.0	1200.0	1300.0	1600.0		Y
Be	5.0	5.0	5.0	6.0		Y
Bi	1.0	nd	0.2	nd		N
Cd	0.5	0.5	nd	nd		Y
Co	42.7	55.0	230.0	290.0	Enriched by crucible	Y
Cr	43.5	343.0	210.0	55.0	Enriched by wall slag	Y
Cu	68.5	72.0	50.0	44.0		Y
F	513.0	30.0	20.0	250.0	Less volatile in lab slag	Y
Hg	1.3	nd	nd	nd		Y
Li	57.5	127.0	110.0	65.0	Enriched by wall slag	N
Mn	261.0	290.0	290.0	370.0		Y
Mo	7.0	18.0	97.0	160.0	Enriched by tube furnace contamination	Y
Ni	60.0	341.0	61.0	31.0	Enriched by wall slag, reduced in lab	Y
Pb	53.9	3.1	1.0	12.0	Less volatile in lab slag	Y
Sb	1.7	0.2	nd	0.3		Y
Sc	59.6	56.0	34.0	40.0		N
Se	10.6	0.2	nd	nd		Y
Sn	5.3	1.1	nd	2.0		N
Sr	1300.0	1300.0	1400.0	1700.0		N
Th	20.5	21.0	18.7	21.8		N
U	5.1	5.7	5.2	5.9		N
V	197.0	194.0	200.0	250.0		N
W	1.5	2.5	1600.0	2100.0	Enriched by crucible	N
Y	61.0	62.0	67.0	75.0		N
Zn	85.0	32.0	8.0	30.0		Y

Table 65: Concentration of trace elements in CRC704 coal mineral matters and their trial and laboratory slags, mg/kg. Bold figures indicate enrichment; figures in blue indicate losses

3.3.4 SLAG LEACHABILITY

Leaching characteristics of the laboratory-produced slags are compared with those of the pilot-scale slags. To minimise uncertainty in leaching characteristics, the two leaching tests (TCLP and ASLP) were performed by one laboratory only (ALS).

The results of these leaching tests are given in Table 66.

	Detection Limit	ASLP test				TCLP			
		CRC701		CRC704		CRC701		CRC704	
		s101	L101	s101	L101	s101	L101	s101	L101
Ag	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al	0.1	0.1	<0.1	0.1	<0.1	28	<0.1	37	<0.1
As	0.001	0.007	<0.01	0.002	0.001	0.003	0.006	<0.001	0.019
Ba	0.01	0.02	<0.01	<0.01	<0.01	1.3	0.02	0.46	0.03
Be	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
B	0.01	0.19	0.07	0.19	0.11	0.21	<0.01	0.22	<0.01
Cd	0.002	<0.002	<0.002	<0.002	<0.002	0.003	<0.002	<0.002	<0.002
Co	0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.01	0.02	0.02
Cr	0.01	<0.01	<0.01	<0.01	<0.01	0.07	<0.01	0.09	<0.01
Cu	0.01	<0.01	<0.01	<0.01	<0.01	0.07	<0.01	0.06	<0.01
Hg	0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Mn	0.01	0.03	<0.01	<0.01	<0.01	0.29	0.02	0.14	0.04
Mo	0.01	<0.01	0.01	<0.01	0.02	<0.01	0.02	<0.01	0.01
Ni	0.01	0.01	<0.01	<0.01	<0.01	0.14	0.03	0.13	0.03
Pb	0.01	<0.01	<0.01	<0.01	<0.01	0.08	<0.01	0.10	<0.01
Se	0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
V	0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	0.03	<0.01
Zn	0.01	0.04	<0.01	<0.01	<0.01	2.6	0.21	0.62	0.10

Table 66: ASLP/TCLP leaching test results for laboratory and pilot scale slags. Red and blue fonts show higher and lower leaching values, respectively, of laboratory slags

Consistent with results for the pilot-scale samples assessed in Section 2, trace elements are more leachable in an acidic buffer solution. However, of interest here is that the concentration of trace elements in leachates from laboratory slags are often lower (blue data) than in the leachates from trial slags, regardless of the extraction methods used. The exceptions are molybdenum, which as discussed, is enriched in laboratory slags due to dissolution of some of the crucible material; and arsenic. An explanation for the arsenic effect will need to be the subject of ongoing work.

The low concentrations of trace elements in leachates from laboratory slags are believed to be due to all laboratory-made slags being in a glassy form, similar to the frit fraction of the pilot-scale slags. As discussed in the Review (Section 3), the leachability of trace elements from the frit fraction of the slags

is generally lower than the leachability of the entire raw slag samples, which contain fine particles and unconverted carbon.

3.4 Conclusions

As seen from Part 1 of this report, the concentration of trace elements in industrial by-products is the primary assessment criteria for their classification for disposal or use schemes. The leachability of trace elements from the material is used for further assessment and classification once this primary assessment has been made. The ability to make such assessments using laboratory-produced slags is of particular interest, due to the general unavailability of 'industrial' slags from the use of Australian coals in a specific gasification technology.

Within this context, the concentration of trace elements in laboratory-made slags is of primary importance. This section has presented trace element compositions of laboratory slags, which indicate that preparation and analysis of laboratory slag from a specific coal can be used for environmental assessment of the coal gasification by-products for the majority of trace element species. For cases in which there was significant variation in terms of elemental concentration in laboratory and industrial slags, the common factor identified was usually contamination of the laboratory slags from the materials used in the laboratory facility. There is considerable scope, therefore, to modify this procedure to reduce these effects. The differences between other elements, such as nickel, chromium and possibly boron, may include their species interaction with gasifier refractory or wall slag. It is also possible that boron is more volatile at the high pressures used in gasification. Analysis of gasifier frozen wall slag may provide better understanding of reactions where the elements listed above were involved.

An initial assessment of the environmental considerations of coals can be based on an ash analysis. However, the concentrations of volatile and highly volatile elements in the slags, including As, Bi, F, Cl, Hg, Pb, Zn, Se and Sb, are much lower than in the parent coal ashes. Some of the trace elements in the industrial slags, such as Ni and Cr, can be enriched by gasifier wall slag. Therefore, trace element evaluation using laboratory-made slags will provide more certainty how gasification slags will comply with environmental regulations.

The procedure for generating laboratory slags can be refined to make it applicable to a wider range of environmentally significant trace elements. Different crucible materials, such as alumina, may be suitable. Generation of slags under less reducing conditions may also be important, in particular for high-iron coals. While the frit fraction of slags can be reasonably well reproduced in the laboratory, other fractions of raw slag, such as fine slag and unburned carbon, are more difficult to reproduce at laboratory scale. Slight modifications to current procedures are unlikely to alleviate this problem. This poses challenges for the general assessment of gasification wastes from a range of gasification technologies and a range of feedstocks, unless we have access to facilities that can reproduce some of the important conditions found in entrained flow gasification technologies.

4 Case Study: Use of gasification slags in the cement industry

4.1 Introduction

The review presented in Part 1 suggested that the characteristics of gasifier slags make them likely candidates for use in the cement industry. However, the lack of experience with characterisation of slags for use in this way makes it necessary to undertake some preliminary testing, to understand how they might satisfy the standards applied in cement industry. The two most feasible applications for slag in the cement industry were considered as supplementary cementitious materials and in concrete aggregates.

Slag aggregate should not be directly substituted for other aggregates in an existing concrete mix. Rather, a mix should be specifically designed based on individual slag characteristics, which is a more time consuming and expensive process than a generic approach for all slags. Furthermore, supplementary cementitious material is a more valuable product than materials in cement aggregates. Therefore, only this approach was considered in this section.

4.2 Characterisation and performance of coal gasification slags

The Cement Australia laboratory was used to characterise a T106 slag sample and estimate its performance as a replacement supplementary cementitious material (SCM) in mortar and concrete production. T106 slag was selected for these tests because it represents slag from an industrial scale (not pilot scale) and because of the quantity requirements from Cement Australia (minimum 15 kg).

4.2.1 SAMPLE PREPARATION AND CHARACTERISATION

Three types of SCM are used in Australia: fly ash, GGBFS and amorphous silica (silica fume). SCMs (pozzolans) are rich in silica and/or alumina. These oxides combine with lime in the presence of water to form compounds that are virtually identical to the compounds in hydrated Portland cement. Standards applied to fly ash and GGBFS for SCM application are used to characterise ground gasification slag.

Before testing, 15 kg of slag was milled to a fineness considered suitable for use as an SCM, thereby approximating fine grade fly ash (as per AS 3582.1: Supplementary cementitious materials for use with Portland and blended cement Part 1: Fly ash) for comparative determinations.

Analyses were carried out as per AS3582.2 (Supplementary Cementitious Materials for use with Portland and Blended Cement, Part 2 – Ground Granulated Iron Blast-furnace). Slag reactivity was determined as per ASTM 1073-97A (Standard Test Method for Hydraulic Activity of Ground Slag by Reaction with Alkali). Goliath GP cement was used for relative water requirement and relative strength determinations.

4.2.2 RESULTS

Slag grindability is based on the number of mill revolutions required to obtain a particle size distribution complying to AS3582.1 (i.e. >75% passing 45 μm) and compared with other products previously used in Cement Australia. T106 slag has a grindability index (GI) of 10 out of 12, which is higher than Bulwer BFS slag (GI=8). Particle size distribution of milled slag is shown in Table 67. Composition of the slag and its mortar properties are listed in Table 68.

Parameter	Slag characteristics
Specific surface area (m ³ /kg)	0.58
Mass median diameter (μm)	12
3 – 32μm (%)	58
> 32μm (%)	21
> 45μm (%)	11
> 90μm (%)	0

Table 67: Particle size distribution of ground slag

Pozzolanic activity of the sample was relatively low compared with a standard fine grade fly ash typically used in concrete. It shows a relative strength of 84% (75% is a minimum), while Tarong flyashes have 90–95%, and BFS has 95–100% of relative strength [8]. However, grinding the slag sample to finer fractions may improve reactivity somewhat. The slag sample was relatively hard, and therefore, grinding costs are expected to be significantly higher than Portland cement clinker and granulated blast furnace slag.

The reactivity test (ASTM 1073-97A) results (Table 69) indicate that similar to granulated blast furnace slag, the tested slag is relatively reactive in contact with an alkaline solution.

Parameter	Slag characteristics	AS – Flyash Specification	BSF slag [8]
Specified parameters			
Fineness, passing 45 µm sieve (%)	91	75 min	
Loss on ignition (%)	2.3	4.0 max	1.2
Moisture content (%)	0.2	1.0 max	
SO ₃ content (%)	0.6	3.0 max	2.5
Available alkali content (%)	0.2	reportable only	
Relative density (g/cm ³)	2.9	reportable only	2.8–3.2
Relative water requirement (%)	98	reportable only	
Relative strength (%)	84	reportable only	95–100
Chloride ion content (%)	0.004	reportable only	
Non-specified chemical composition, wt%			
SiO ₂	46.1		
Fe ₂ O ₃	22.4		
Al ₂ O ₃	15.7		
CaO	13.4		
MgO	1.8		
TiO ₂	0.8		
P ₂ O ₅	0.5		
Mn ₂ O ₃	0.5		
Na ₂ O	0.36		
K ₂ O	0.30		

Table 68: Chemical composition and mortar properties

Material	Reactivity, MPa
T106 grouted slag	22.6
Tarong flyash	0.1
Port Augusta flyash	6.6
Bulwer (GBFS) slag	26.2

Table 69: Comparative reactivity data

4.3 Slag grindability and microhardness

The results of the previous section indicate that slag grindability could be a potential issue for its use as a supplementary material in the cement industry. Slag grindability depends on the bulk characteristics of raw slag, such as fractions of coarse (frit) and fine slag, as well as intrinsic characteristics of the coarse slag, such as microhardness. Relationships between microhardness and grindability have been investigated for various materials, including metals, composite materials, coals, minerals and cement clinkers [9–14]. ‘Vickers Hardness Test’ has been used to characterise the mechanical properties of commercial clinkers and blast furnace slags [14, 15].

In this study, the microhardness of four slag samples was determined using the Vickers Hardness Test, to evaluate possible differences in grindability of gasification slags. Tests were conducted on two pilot-scale slags, s101 and s104, and two frits from industrial slags, T105 and T106.

Microhardness testing is indentation hardness testing that involves forcing a precisely shaped polished diamond indenter (Vickers) of specific geometry into the surface of the test material, at loads ranging from 1 to 1000 g. Hardness is evaluated by measuring the size of the resulting unrecovered indentation using a microscope and established formulae. The details of the testing procedure can be found elsewhere [16].

In this present study, microhardness tests were conducted using a Micro-Vickers Hardness Tester. The Vickers indenter is a square-based pyramidal diamond with face angles of 136° and it produces an indentation with the depth of about one-seventh of diagonal length. The measurement process is a fully automatic operation, from applying load to holding and releasing. Load applied for all tested samples was 100 gf (100 gram force or 0.98 N).

The Vickers hardness number (HV) is the ratio of the load applied to the indenter to the surface area of the indentation:

$$HV = 2P \sin\left(\frac{\theta}{2}\right) / D^2$$

where P is the applied load, kgf; D is the mean diagonal of the indentation (mm) and θ is the angle between opposite faces of the diamond (136 °).

Tests were conducted for at least three pieces of each slag sample, and the microhardness of each piece was measured three times in three different areas. Results of the test are listed in Table 70.

Sample	Micro-hardness, HV
s101	508–668
S104	669–926
T105	988–1158
T106	702–767

Table 70: Microhardness of slag samples

Since a limited number of measurements were made for each slag sample, the results are only indicative. However, they demonstrate that slag microhardnesses of the four test samples were different, even with variation of the values for each slag. T106 slag, the grindability of which was relatively high, has medium values of the hardness within four tested slag samples and less variation in microhardness values. The differences in microhardness of the tested slags are likely associated with their chemical composition and processing conditions. These relations can be established through complex research work and with a significantly greater number of the slag samples produced from coals with different ash compositions and at different conditions.

The relations between microhardness and grindability are also complex, and some other microcharacteristics of the materials that affect grindability have to be considered. More slag characterisation is required to establish relations between micro and macro-properties of the slag that can be used to evaluate slags for particular applications.

4.4 Conclusions and recommendations

Gasification slag is unique in terms of its compliance to Australian standards: it does not quite fit into the categories of GGBFS (AS 3582.2) or fly ash (AS 3582.1). Regarding 3582.2, this standard clearly refers to granulated slag from an ‘iron blast furnace’. Additionally, the FeO content of the gasification slag is well above the allowable limit for iron, which is $\leq 1.5\%$. The high FeO content will also impart a red/brown colour to concrete and mortar. Regarding AS 3582.1, the gasification slag chemistry matches that of a Class C Fly Ash (Class C Fly Ash: $\geq 10\%$ CaO & $\leq 55\%$ (Al₂O₃ + SiO₂)), which is not available in Australian concrete. However, AS 3582.1 (3.1) clearly states that ‘Fly ash is a solid material extracted from the flue gases of a boiler fired with pulverized coal’. Furthermore, ‘The term does not apply to ash extracted from the bottom of a boiler (furnace ash) or economizer grits’.

Widespread use of gasifier slag would be restricted, due to lack of detailed understanding and long-term durability studies. The latter require comprehensive testing and specification of the material to fully meet current infrastructure standards. This would certainly be the case if slag is considered for use in any infrastructure work involving government authorities. Engineering and durability concerns will need to be addressed so that the technology meets the requirements of the relevant standards.

Cement Australia suggests that there may be scope to use the by-product in alternative concrete binders, such as geopolymers, since the tested slag is reactive in contact with alkaline solutions. The use of geopolymers is still limited in the concrete industry. However, alternative ‘green’ binders will gain more prominence since the introduction of the federal carbon tax. In this regard, there may be scope to use gasifier slag in alternative binders, although restrictions for use, in view of the lack of relevant standards and specifications, will still be an impediment.

5 Laboratory work: Conclusions and recommendations

Environmental assessment of slags and other by-products is an essential component of the development of appropriate strategies for their disposal or use. This part of the report has presented the analysis and characterisation of by-products of industrial-scale entrained flow gasification processes, and made some preliminary assessments of the potential classification of by-products in waste disposal schemes of different Australian states. This work has also investigated the suitability of laboratory-made slags for use assessing the environmental performance of by-products in the absence of industrial slag.

Waste materials are classified by their total concentration of trace elements and their leachability. This often leads to an unrepresentative classification of gasification slags, as there is no link between concentration of trace element species and their leachability. This issue is further confused by the uncertainties associated with differences in the test procedures. These likely reflect the strong pH control on element uptake, which is similar to that found in previous studies of pf fly ashes [17]. While the majority of species are low-leaching, and are therefore unlikely to pose any environmental or use barrier, some slags are otherwise classified. More work in understanding the coal and technology-specific behaviours and characteristics of gasification by-products is required. The environment in which by-products will be disposed or used is also important. Therefore, further research is required to determine the most appropriate leaching test procedures for specific disposal or use schemes.

The laboratory results also demonstrate that the lack of knowledge of slag characteristics, and how these depend on parent coals and gasification conditions, narrows the field of its application. The case study for use of slags as supplementary cementitious material highlighted the importance of understanding the relationships between slag bulk properties and intrinsic characteristics, such as hardness.

Potential fields of research into identifying and characterising by-products for disposal and use include:

- linking coal characteristics and gasification conditions with slag physical and chemical properties
- effect of gasifier wall materials and frozen slag on characteristics of tapped slag (e.g. slag-refractory interactions)
- linking intrinsic slag characteristics (hardness, alkanity, chemical and phase composition) with the macro-characteristics of slag as a raw (precursor) material.

The lack of data and samples from gasification of Australian coals under realistic entrained flow conditions mean that these programs will need to run in parallel with other experimental gasification research activities.

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Part III: Key Outcomes

1 Key outcomes

This work has presented a detailed analysis of legislation, regulations, data, and samples relevant to gasification by-product management in an Australian context. This will help Australian regulators and prospective IGCC-CCS project proponents to define and meet their obligations for managing solid wastes from gasification-based plants. The review and subsequent laboratory work identified the key issues of current international practices, and potential Australian practices, associated with disposal and use options of coal gasification by-products. Together, they offer guidance for future work required to reduce the risks of deploying Australian gasification-based coal-fired power generation systems.

1.1 Disposal of gasification by-products

1.1.1 LEGISLATIVE AND REGULATORY ISSUES

While IGCC or gasification by-products are not specifically mentioned in current Australian legislation, they are likely to be assessed in the same manner as coal combustion products, such as fly ash and bottom ash. Relevant legislation is therefore based mostly on handling and disposal of fly ash, and lacks a sound scientific basis regarding the characteristics and behaviour of slags from entrained flow gasification. Furthermore, regulations for solid wastes vary significantly from state to state, resulting in different hazardous element specifications, concentration limits and leaching requirements.

In all states and territories, assessment of waste leaching characteristics is based on the toxicity characteristic leaching procedure (TCLP) and Australian Standard Leaching Procedures (ASLP, an Australian version of the TCLP) tests. However, not all states have specified the conditions to be applied in these tests (such as pH). This can cause significant differences in the classification of materials.

State and territory legislation varies considerably. A more uniform, national approach is required, based on sound scientific information regarding material characteristics, test conditions, and their relevance to the target disposal or use scheme.

1.1.2 BY-PRODUCT PERFORMANCE

Knowledge of slag characteristics from gasification of Australian coal is limited. This is due to the absence of full-scale or large pilot-scale gasifiers in Australia, and the challenges associated with sourcing slags from other pilot-scale gasification operations. This work has characterised gasification by-products from Australian coals using some of the limited number of samples obtained from recent research programs.

Results indicate that these gasification slags and fly ashes are generally low-leaching materials, as assessed by common regulative leaching tests (ASLP and TCLP). Their classification in Australian regulations is likely to be mainly affected by their total concentration of trace elements; only in some cases are leaching characteristics more important than the total element concentration. This has the potential to require more stringent environmental or use considerations than may be required based on the low leachabilities of these trace element species.

These outcomes, however, cannot cover the range of Australian coals and the gasification technologies in which they may be used. A representative database on coal slag characteristics is needed. The database should include specific feed coal characteristics and the influence of gasifier operating conditions. Using characteristics of laboratory-made slag could extend the database. However, real gasification by-products from gasification of Australian coals are still required to cover limitations of the laboratory-made slag fabrication process, as not all aspects of trace element behaviour are well represented in the laboratory.

1.2 Slag use opportunities and challenges

Gasification slags produced from IGCC plants worldwide are used in applications such as cement manufacturing, road base and structural backfill. The most immediately prospective application of IGCC slags from Australian coals would appear to be in the cement industry and some road base applications. These and other value-added use options are all technically feasible, but are likely to face some challenges associated with:

- a lack of relevant standards for the use of gasification slags in a particular application
- the small size of the potential Australian market
- transportation and processing costs.

The lack of specific standards is compounded by the lack of local experience in the use of gasification residues. For example, Australian gasification slags do not always satisfy existing standards that are applied to the use of blast furnace slag (e.g. AS 3582.2 applied to ground granulated blast furnace slag).

This may impede some opportunities for using gasification by-products. While gasification slags have similar chemical and phase compositions to fly ashes, the slags are generally more chemically stable. Their physical appearance is also different from fly ashes, and they therefore have to be used differently in industrial fly ash applications. This may cause some difficulties in assessing slag use options, since slags are not well represented by fly ash standards (AS 3582.1).

Laboratory work has demonstrated that the lack of knowledge of gasification slag characteristics – and how these depend on fuel properties and gasifier conditions – also narrows the field of its application. Results obtained in the case study for practical use of slags as supplementary cementitious material, for example, indicate that issues such as relative strength and grindability are critical. Yet, there is very little understanding of the relationship between such slag bulk properties and intrinsic characteristics, such as microhardness, alkalinity, chemical and phase composition.

The state-of-the-art of coal combustion by-product use was covered extensively in the report on survey commissioned as part of this project (attached as an appendix to this report). An important recommendation of this report is that: ‘a thorough understanding of the logistics and subsequent economic value of the material on a case-by-case basis is necessary before undertaking such an endeavour. However, note that despite the potential lack of viability in some geographical regions, research into the field is strongly advised, as government regulation of waste disposal and carbon taxing are plausible scenarios. These scenarios would act as significant drivers to further development of the ash and slag utilisation industry’.

Appendix:

Use of Power Station Ash & Slag: Review of Australian Practice

Industry Consultant Report



ULTRA-SYSTEMS TECHNOLOGY PTY LTD

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CONFIDENTIAL

Use of Power Station Ash & Slag

Review of Australian Practice

Final Report

prepared for

CSIRO Energy Technology

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COVER SHEET

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Review of Australian Practice

Report No: c1351

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PO Box 883
Kenmore QLD 4069

Authorisation: Sub-contract to provide services to CSIRO, dated 5/09/11.

Prepared by: Justine van der Werf, Mechanical Engineer
Lindsay Juniper, Thermal Coal & Power

Date: 27 March 2012

Signed.....

A handwritten signature in blue ink, appearing to read 'Lindsay Juniper', written over a dotted line.

Lindsay Juniper
Director

Use of Power Station Ash & Slag

Review of Australian Practice

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EXECUTIVE SUMMARY

This report examines the current state and the future viability of the slag utilisation industry in Australia. The main objectives of this review are:

- Provision of a current practise overview in disposal schemes for coal combustion products (CCP), including fly ash, bottom ash and slag in Australia;
- Provision of a current practise overview on CCP utilisation for industrial application (cement industry, road base application, others);
- Provision of key current regulation and permitting requirements and their impact on strategies and procedures for CCP disposal and utilisation;
- Identification of prevailing barriers for CCP application in Australia with reference to differences between States and the probable facility of current utilisation industries and regulations to accommodate gasification derived slags.

The case studies and the legislation covered in this document illustrate that the logistics surrounding an ash producing operation greatly impact upon the viability of any ash utilisation project and is perhaps one of the greatest contributing factors. Areas of logistical importance include; proximity of the ash generator to a consumer market, proximity to ash utilisation industries such as cement works and transport facilities and modes of transport.

Other areas of importance include factors such as ash quality, leachate concentrate levels, technical level held by potential utilisation industries in the area, ash handling facilities onsite and government legislation and taxing. Current legislation is supportive of ash utilisation schemes, and any introduction of carbon taxing or waste disposal taxes would prove to be drivers for increased viability of the ash utilisation enterprise.

Recommendations from this report suggest that a thorough understanding of the logistics and subsequent economic value of the material on a case by case basis is necessary before undertaking such an endeavour. However, note that despite the potential lack of viability in some geographical regions, research into the field is strongly advised as government regulation of waste disposal and carbon taxing are plausible scenarios. These scenarios would act as significant drivers to further development of the ash utilisation industry.

GLOSSARY OF TERMS

AAC	Autoclaved aerated concrete
AAS	Atomic absorption spectrometry
ACAA	American Coal Ash Association
ALF	Accelerated Loading Facility (Australian Roads Research Board)
AMD	Acid mine drainage
ANZECC	Australian and New Zealand Environment Conservation Council
AOC	Approximate original contours
ARD	Acid rock drainage
ARPANSA	Australian Radiation Protection and Nuclear Safety Agency
ASTM	American Society for Testing and Materials
BIE	Bureau of Industry Economics
CANMET	Canadian Centre for Metallurgy
CaOH	Hydrated lime
CBR	California bearing ratio
CCAA	Cement Concrete and Aggregates Australia
CCB	Coal combustion by-product
CCP	Coal combustion product
CCSD	Cooperative Research Centre for Coal in Sustainable Development
CCUJ	Centre for Coal Utilisation of Japan
COAG	Council of Australian Governments
CRC	Cooperative research centre
CSF	Cement stabilised fly-ash
CVAAS	Cold vapour atomic absorption spectrometry
EC	Electrical conductivity
ED	Energy-dispersive (spectrometry)
EPHC	Environment Protection and Heritage Council
ESA	Equivalent standard axle
ESP	Electro-static precipitator (also: exchangeable sodium percentage)
FAAS	Flame atomic absorption spectrometry
FBA	Furnace bottom ash
FGD	Flue gas desulphurisation
GBFS	Granulated blast furnace slag
GFAAS	Graphite furnace atomic absorption spectrometry
GHG	Green-house gas
HVFA	High-volume fly ash
ICCP	International Committee for Coal and Organic Petrology
ICP-MS	Inductively coupled plasma atomic emission spectrometry
IGCC	Integrated Gasification Combined Cycle
IP	Intellectual property
LMC	Lean-mix concrete
LOI	Loss on ignition
LTA	Low temperature ash
LWA	Lightweight aggregate
MRET	Mandatory renewable energy target

NATA	National Association of Testing Authorities
NEPM	National environment protection measure
NO _x	Nitrogen oxides
NPI	National Pollutant Inventory
OMC	Optimum moisture content
OSM	Office of Surface Mining (US)
PAH	Polycyclic aromatic carbon
PF	Pulverised fuel
PFA	Pulverised fuel ash
ppm	Parts per million
R&D	Research and development
RTA	Roads and Traffic Authority of Australia
SAI	Strength activity index
SAR	Sodium adsorption ratio
SEM	Scanning electron micrograph
SGLP	Simulated groundwater leaching protocol
SI	Saturation index
SPLP	Synthetic precipitation leaching procedure
TCLP	Toxicity characteristic leaching protocol
TEM	Transmitted electron microscope
UCS	Unconfined compressive strength
UKQAA	United Kingdom Quality Ash Association
UTS	University of Technology, Sydney
WD	Wavelength-dispersive (spectrometry)
XRD	x-ray diffraction
XRF	x-ray fluorescence

REPORT

1 INTRODUCTION

The proposed Australian IGCC-CCS (Integrated Gasification Combined Cycle – Carbon Capture and Storage) demonstration projects are anticipated to produce sizable quantities of slag. These by-products have no historical background in commercial-scale coal gasification plant in Australia, and subsequently there is concern associated with the uncertainty of permitting, licensing, and technical requirements for the stowage, disposal, management and handling of these materials.

This report addresses some of these uncertainties. There are few IGCC plants of commercial generating capacity in the world. The utilisation practices that are in place at these plants are addressed as are the current regulatory and permitting requirements associated with the slag waste utilisation. The main objectives of this review are:

- Provision of a current practise overview in disposal schemes for coal combustion products (CCP), including fly ash, bottom ash and slag in Australia;
- Provision of a current practise overview on CCP utilisation for industrial application (cement industry, road base application, others);
- Provision of key current regulation and permitting requirements and their impact on strategies and procedures for CCP disposal and utilisation;
- Identification of prevailing barriers for CCP application in Australia with reference to differences between States and the probable facility of current utilisation industries and regulations to accommodate gasification derived slags.

An IGCC plant produces three categories of solid waste. These are a dense slag, elemental sulphur, and small quantities of solid captured on process equipment (MIT, 2007). The slag is dense and vitreous and allows for difficulty in leaching (MIT, 2007). Note must be made however, that evidence has been found in long term leaching studies indicating release of contaminants in coal gasification slag (EPRI, 1989). This leaching work needs to be further considered; it establishes that engineering controls shall need to be applied to IGCC combustion products in order to ensure adequate protection of surface and groundwater reserves.

Solutions for ash utilisation are necessary as legislation is becoming tighter in the disposal arena and as depicted in Figure 1.1, which shows the estimated solids emissions (ash production) for three electricity supply scenarios with supply demand to increase by 2.5% pa (ADAA, 2008). As shown, there is likely to be a doubling of stored and managed ash before 2050.

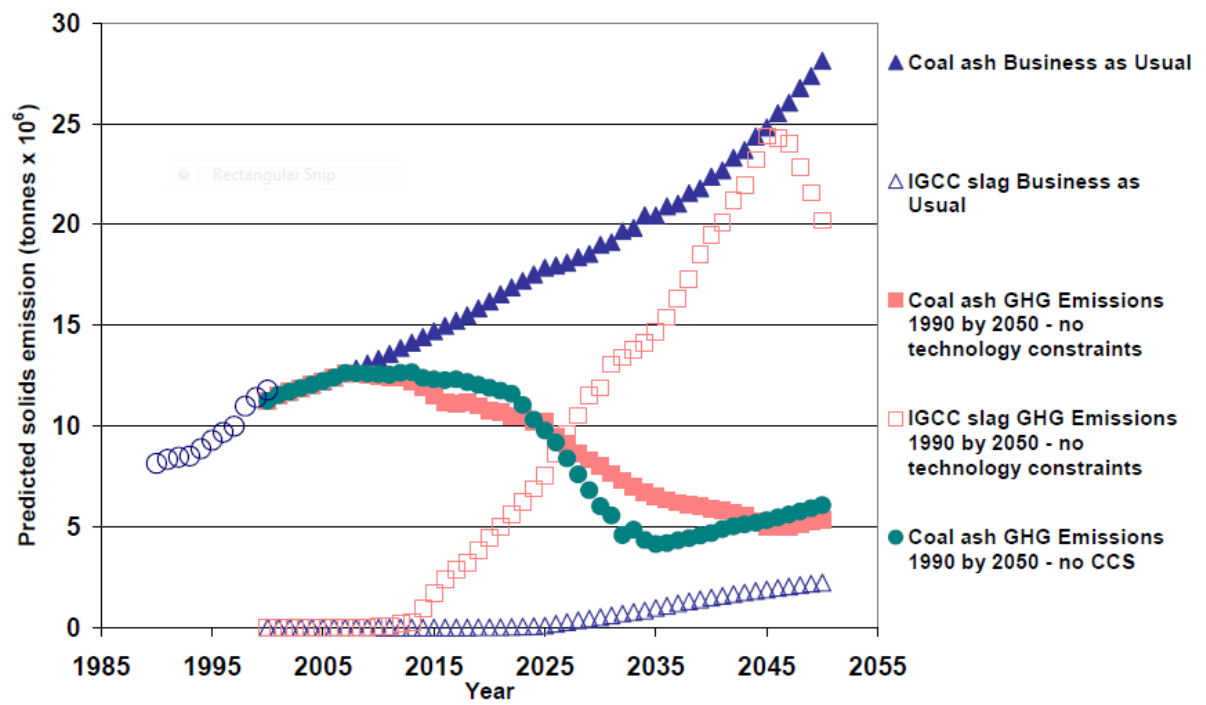


Figure 1.1: Predicted solids emissions 2000-2050

2 BEST PRACTICE FOR DISPOSAL SCHEMES

2.1 INTRODUCTION

CCPs (Coal Combustion Products) produced from coal-fired power stations embody an opportunity for utilisation as a useful raw material for a range of industrial products.

In 2010 approximately 14.1 million tonnes of CCPs were produced in the Australasian region. Of this about 5.8 million tonnes; or 41% was effectively used to some beneficial end; and about 1.9 Mt or 14% was used in high value-added applications such as cement applications or concrete manufacture. The majority, at about 24%, was used in projects that typically generate no economic return, but do supply cost avoidance or recover; such projects include onsite mine remediation and local haul roads. Surplus CCPs are typically placed into on-site storage ponds. This represents about 59% of total CCP generation. (HBM Group Pty Ltd, 2010)

This section investigates current best practice for disposal schemes in Australian, and at 59% disposal represents the largest portion of CCPs.

Innes and Davies (2000) appraised both past and current practices for ash disposal relevant to Australia and abroad. They attested that at the time of publication, the 15 years preceding had exhibited a gradual modernisation of disposal practices with an inclination from wet pond to dense phase and dry disposal. This trend was the likely result of better understanding in the field of leachates and the introduction of increasingly rigorous legislation.

For example, Millmerran Power Station advanced from the standard custom of ash dam disposal to void filling. The justification by the designers, Sinclair, Knight Mertz (SKM), was that by employing the ash to void fill, they in essence were entombing the ash in the mine, slightly beneath the root line of plants and considerably above groundwater level, forming a cement sandwich which would avoid leachate seepage into the water supply and damage the flora. They viewed this as more sustainable, and further it addressed the following three fields (Nelson, 2008):

- Social sustainability: by allaying environmental fears held by the local community;
- Environmental sustainability: by avoiding water pollution and flora damage which would likely have subsequent fauna ill-effects;
- Economical sustainability: by reducing the cost of ash dam creation and maintenance.

This trend towards dry disposal may also result from the requirement for redevelopment and expansion of existing ash handling and storage facilities.

2.2 TYPES OF CCP DISPOSAL IN AUSTRALIA

Where re-use is not an option for whatever rationale, there are a number of disposal opportunities. Of these some widespread approaches include:

- Controlled structural fills for coal ash;

- Moist ash processing and dewatering basins;
- Dry ash storage and landfills;
- Dry ash storage and landfills;
- Moist ash storage and landfills;
- Mine backfill; this can be either dry or moist fill as in the categories above and as indicated in the study by Ward et al (2006) can be directed towards a number of objectives including stabilisation, sealing, reclamation, rehabilitation, among others.

These can be broadly grouped into two sections, placement into landfill and placement as mine backfill. In the case of ash placement into landfill there is an increased use of dense phase and dry ash placement ver wet disposal. This is reflected in the redevelopment of existing ash handling and storage facilities. This is portrayed in Table 2.1; dry and dense phase disposal is partly driven by the concerns associated with trace element leaching and the introduction of legislation mandating ‘zero discharge’ (Nelson, 2008).

Table 2.1: Ash disposal methods since 2000

Power Station	Construction Date	Nominal Output (MW)	Disposal Method	Additional comments
Callide C	2001	900	Dense phase	
Millmerran	2003	840	Dry	Mine infill
Tarong North	2003	445	Wet	Moving to dense phase mid 2008
Kogan Creek	2007	200	Dense phase	Co-mixing with bottom ash and overburden and disposal to mine void later in project
Blue Waters 1	2008	200	Dry	Co-mixing with bottom ash and overburden and disposal to mine void

2.3 ASH PLACEMENT CASE STUDY: MINE BACKFILL

In 2008, the use of void back-filling was justified for use at Millmerran Power Station. The justification was made by SKM and it suggested that the need to backfill arose from community concern regarding the usual practice of disposing ash into an ash dam. The concern was that such a practice could result in groundwater contamination.. (Nelson, 2008).

This disposal method buries the ash back into the mine below the line of plants and well above the ground water level. This forms a ‘cement sandwich’ which does not leach into the water the supply nor damage the flora above. It additionally serves the community by alleviating social concerns, and economically the project reduces cost of creating an ash dam.

Another instance of a mine backfill application is cited in the 2005 report by the Environmental Protection Authority (EPA) () on the then proposed Bluewaters Power Station in Western Australia.

In 2004, Griffin Energy submitted a proposal to the EPA requesting development of the Bluewaters Power Station including ash disposal to a mine void. The key characteristics of

the relevant to the request are outlined by Table 2.2. From the proposal document (the PER document) as submitted by Griffin Energy, the ash and mine overburden were to be disposed into the mine voids above the water table. This was found to fix the trace elements within the ash by reaction with clay. The EPA in their responding report (EPA, 2005) noted that this same method was being utilised by Bayswater Power Station in New South Wales. They also noted that the disposal of ash into mine voids has the potential to increase groundwater salinity and may lead to some contamination of ground water. The proponent's commitments to address these matters were as follows:

Commitment 9 Action Items:

- 1 Develop and implement a waste management plan as part of the operational phase EMP;
- 2 Develop and implement a fly ash management plan as part of the operational phase EMP.

In both of these cases, mine backfill was deemed to be socially, economically and environmentally beneficial when compared to purpose built dry or wet storage facilities.

Table 2.2: Key proposal characteristics for Bluewaters Power

ELEMENT	DESCRIPTION
General	
<ul style="list-style-type: none"> Project Purpose: Construction Period: Project Life: Project Value: Power Plant Type: Power Generating Capacity: Plant Thermal Efficiency: Plant Operation: Shutdown Time: Maximum Facility Footprint: Maximum Total Area: 	<ul style="list-style-type: none"> To produce electricity to supply to the SWIS grid or direct to customers 30 months to commercial operation 30 years Approximately A\$200 Million Subcritical coal fired power station Up to 200MW_e nominal, 202.3MW design HHV 36.4% - LHV 38.6% Base load operation 24 hours per day, 365 days per year Plant maintenance shutdowns may be scheduled annually 350m x 150m area 15 hectares
Plant Facilities	
<ul style="list-style-type: none"> Stacks: Height of Stack: Diameter of Stack: Cooling Towers: Liquid Fuel Storage Tanks: Boiler: Steam Turbine: Wastewater collection: 	<ul style="list-style-type: none"> 1 100m 4.13m 1 set 2 x 100,000 litres and 1 x 10,000 litres Balanced draft pulverised coal steam generator matched to steam turbine capacity Tandem compound reheat steam turbine with synchronous alternator – 200MW_e Package treatment plant
Utilities	
<ul style="list-style-type: none"> Water Supply: Coal Supply: Transmission Line Length: 	<ul style="list-style-type: none"> 3.25GL/yr sourced from mine dewatering at Ewington 1 0.7Mtpa via conveyor owned and operated by Griffin Coal Mining Company 100m up to 3km depending on interconnection point as required by Western Power
Emissions	
<ul style="list-style-type: none"> Noise: Fine Dust: Nitrogen Oxides: Sulphur Oxides: Greenhouse Gases: Carbon Monoxide: Volatile Organic Compounds: PAHs: Arsenic: Cadmium: Chromium compounds: Lead compounds: Mercury: Fluorides: POPs inc. Dioxins and Furans: 	<ul style="list-style-type: none"> Less than 60dB(A) at 150m from the plant. Less than 29dB(A) at nearest residence in Collie 47mg/Nm³ at 7% O₂ dry basis; 9g/s; 227tpa 606mg/Nm³ at 7% O₂ dry basis; 121g/s; 3050tpa 1490mg/Nm³ at 7% O₂ dry basis; 296g/s; 7470tpa 1,300,000tpa CO₂ e 500mg/Nm³ at 7% O₂ dry basis; 93g/s; 2350tpa 32kg/yr 6.0kg/yr 6.7kg/yr 8.5kg/yr 1.5kg/yr 31kg/yr 31kg/yr 17,000kg/yr (instantaneous rate estimated to be less than 590mg/s) Less than 0.5 grams per year
Waste	
<ul style="list-style-type: none"> Ash: Septage: Saline Water: 	<ul style="list-style-type: none"> 175,000tpa disposed to the adjacent mine (Ewington 1) Package treatment plant 1.2GL/yr
Workforce	
<ul style="list-style-type: none"> Construction: Operations: 	<ul style="list-style-type: none"> Approximately 150 personnel at the peak of construction Up to 30 full time operations and maintenance personnel

2.4 ASH PLACEMENT CASE STUDY: LANDFILL

In September 2009, SKM finalised a report for the Mt Piper Power Station Ash Placement Project (SKM, 2009). The purpose of the report was to support Delta Electricity's concept

application for the Mt Piper Ash Placement Project. At the time, Delta only utilised about 18% of the ash it generated; the remainder flowing to dry ash repositories. It was conditioned to about 20% moisture and compacted in stockpiles. The primary cause of this high disposal rate was lack of market for the product. Studies are underway to modify the product such that it may become more desirable to potential buyers (Flood, 2011). However, as the situation presented itself in 2009, Delta Electricity was in a position that necessitated the extension of its ash repository system. This case study briefly touches on the best practice for such a repository design and execution. First, the ash repository system present at the time of the report will be briefly examined, this area was known as Storage Area 1.

2.4.1 Existing ash storage

Storage Area 1 was an open cut mine void located on the north east side of the power station. The practice of dry ash storage usually involved placement to the desired height in 'pads' of ash built to the desired height. Ash, that had been moisture conditioned with water, were placed at lower layers to an elevation of 946m and ash conditioned with Brine placed above this level (SKM, 2009).

The ash is placed in half meter layers and is compacted to 95% of its initial mass through a combination of controlled addition of water and a process of machine compacting with the use of rollers and rubber tyred vehicles, which are also used for the transportation of the ash product. Ash is layered and stepped to produce a batter slope of 1(V):4(H), with benches each 10 meters in vertical height change.

For long term pads on the final layers, the final surface was graded to 1% to drain surface water away. For working pads, the surface was graded to 2% along the pad length. At each 10m height interval, a 10m bench was constructed on the batters that were to remain as permanent boundaries. Surface water runoff is always drained away from permanent batters and directed to flow along benches and/or formalised canals. Runoff typically is directed to the centre of the ash placement area where runoff water can be directed to dirty water storage. If this is not plausible it is discharged down batters in lined channels to minimise damage.

At the completion of each pad the area is progressively covered by mine spoil and revegetated

2.4.2 Proposed ash disposal system

There are key environmental considerations associated with the design and approval of such an ash placement project and detailed environmental assessments are required to support an application to the Minister for Planning under Section 75D of the Environmental Planning and Assessment Act 1979 (EP&A Act) for concept approval. Under the EP&A Act, Section 75B, such a project is deemed to be a major project and the Director General of the Department of Planning is required to issue the Environmental Assessment (EA) requirements as per Section 75F of the EP&A Act.

Preliminary investigations undertaken for the proposal identified that the key environmental issues for Mt Piper Power Stations Ash Placement included (SKM, 2009);

- Air Quality; Air Quality conclusions found that construction activities were potential sources of nuisance dust emissions. A comprehensive air quality assessment was required to identify level of risk and relevant mitigation strategies;
- Water Management; Water management includes rainfall and site geology, runoff and flood risk. Detailed analysis is necessary to ensure no impact upon the ecology or drinking water catchment is resultant. A detailed investigation is required;
- Noise; The preliminary noise assessment found that the expected noise emissions would be unsatisfactorily high and noise impacts would require detailed modelling in accordance with industry recognised standards and protocols. Criteria used for assessment is developed in accordance with the NSW Industrial Noise Policy;
- Cultural Heritage; Cultural Heritage assessments and consultation with local Aboriginal groups was identified to be necessary as part of the Environmental Assessment. Appropriate management plans were identified as necessary during construction works and operation. Any significant sites and items would require salvation;
- Visual Amenity; A visual impact assessment was required which involved analysis of existing photographs, maps and drawings, a survey of sensitive locations, graphical stimulation of the proposed placement and development mitigation measures planned to reduce the visual impact;
- Ecology; Ecology was found to be effected by the proposed new sites. The proposed methodology for ecological assessment was to be conducted in accordance with the DECCW 2004; “Threatened Biodiversity Survey and Assessment: Guidelines for Developments and Activities”.

Delta was seeking approvals for four placement sites and, subsequent to being granted concept approval, sought project approval for placement. Detailed studies are required to be undertaken, as above, for each of these in the environmental assessment for this to occur.

Other environmental issues were deemed to be secondary but would be investigated in the full environmental assessment.

Ash would continue to be treated as per existing operations. Fly ash is treated to give 15% moisture to facilitate transportation and minimise fugitive dust, and to aid compaction during ash placement. Brine is used to treat the ash and becomes immobilised within ash pores. The brine conditioned ash is placed only above level RL 946 meters. Below this point, the fill is water conditioned; both brine and water act against fugitive dust emissions. The surface dampness is maintained with a combination of a spray system and mobile water tanker. The ash pad compaction system utilised would further be applied to the proposed sites.

From a legislative perspective, the disposal project is not governed by Commonwealth legislation as under Commonwealth legislation, the only waste regulations are those indicated under the Basel Convention and this coal ash does not have the waste characteristics described under that convention. Under NSW legislation, it is not classified as a waste facility as it receives and stores ash in excess of 20,000 tonne from electricity

generation plants, and also because the material is non-hazardous (Riley, 2005). Thus, there is no ash disposal specific legislation pertaining to the project, only the standard environmental planning assessments, and they fall into the following State Environmental Planning Policies:

- SEPP 44 – Koala Habitat Protection;
- SEPP 55 – Remediation of Land;
- Drinking Water Catchments Regional Environmental Plan No.1;
- Sydney REP No. 20 – Hawkesbury – Nepean River (No.2 – 1997).

The area is located within the Lithgow Local Government Area and is subject to the *Lithgow City Local Environmental Plan 1994*. Within this, the development site would be permissible with consent.

Commonwealth approval from the Minister for Environment is also required as described in the *Environment Protection Biodiversity Conservation Act 1999*.

2.5 DRIVERS AGAINST DISPOSAL

Many international regulators impose levies on ash being disposed of in preference to application of the ash as a product. The risk exists that a privatised electricity market may lead to treatment of ash as landfill and subsequently like and other landfilled waste (Nelson, 2008).

The NSW government strategy infers that “valuable resources continue to be lost through the disposal of waste rather than its recovery for recycling and reuse. Major objectives of the Government’s waste strategy are waste minimisation and recycling” (Nelson, 2008).

Overall the primary drivers against disposal are as follows:

- Current and future legislation;
- Leaching concerns;
- Storage capacity;
- Storage maintenance cost;
- Future land management and rehabilitation costs;
- Impact on surrounding wildlife and risk of animals entering the area (A study was undertaken on a quantitative assessment of ecological risk using metal concentrations in ash, surface water, small mammal and vegetation (Kosson DS, et al, 2002). They found that for some species, the metal levels may be detrimental to survival and reproduction);
- Risk of increased cost of disposal.

An additional driver against disposal is the life expectancy of many stations presently in existence around Australia. These stations, when faced with the option to build further storage capacity, may find that utilisation is a far more worthy cost alternative.

3 BEST PRACTICE FOR CCP USE IN INDUSTRIAL APPLICATIONS

3.1 SOURCES & PRODUCTS

Disposal of coal combustion products (CCP) such as fly ash and bottom ash is an expense, a potential long-term liability and can be logistically unfeasible. There are increasingly stringent regulations affiliated with ash disposal which require higher levels of investment and preparation. Additionally, note must be made of the impending taxes concomitant with the production of energy; its application and by-products (Department of Climate Change and Energy Efficiency, 2010). Hence, due to these concerns CCP utilisation has a number of advantageous characteristics in conjunction to the prospective revenue to be derived of it.

The traditional CCP utilisation market in Australia is dominated by the cementitious products market, and currently dominates CCP utilisation practices. Non-cementitious products in the market include fly ash as an asphaltic concrete filler, furnace bottom ash as a sand replacement in building construction, underground mining and agriculture as well as occasional use as bulk fill in civil engineering works, and mine site rehabilitation for both fly and bottom ash.

In all utilisation schemes, the responsibility of assessing the viability of CCP or slags falls to whichever party is the driver for the project. Where power-stations see the viability of CCP utilisation, they fund research projects to that effect; as was the case in the Tarong cenosphere project. However, companies, such as Adbri Masonry and Cement Australia, drive a number of ash utilisation projects and research organisations have also had a history of input.

As gasification derived slag is currently not a generator level by-product in Australia, current best practice can be based on fly ash and bottom ash utilisation, though overseas slagging gasifier waste utilisation is briefly investigated in this review, as well as iron blast furnace slag, which has physical properties analogous to that of coal gasifier derived slag.

Current access to these markets is limited by cost of transport; this is a key issue in the economics of ash utilisation. Where ash must be dry, this can require use of sealed pneumatic tankers to avoid ash contamination to the environment and loss of product on route. Due to large distances between stations and populations centres in Australia, transportation is especially relevant as a barrier. Table 3.1 (CCSD, 2007) illustrates this by tabulating fly ash production and use in various countries.

Table 3.1: Fly ash production and use comparison

Country	Year for data	Production (kt)	Proportion Used (%)
Australia	2002	12,500	32
Canada	2002	4,744	21
China	2002	150,000	66
Denmark	2002	729	98
EU15	2002	43,047	89

Country	Year for data	Production (kt)	Proportion Used (%)
India	2001-2002	100,000	23
Israel	2000	1,300	98
Japan	2002	9,300	83
Netherlands	2003	996	100 (demand greater than supply)
South Africa	2002	22,000	30
UK	2002	5,500	55
USA	2002	76,500	35

Once transport has been resolved another barrier is competition. Producers of CCPs such as fly ash and bottom ash must compete with quarries and sand mines for applications in cement and concrete products as well as the aggregate market and in some cases fill markets. The major companies in the ash products market sell in excess of 50,000 tonnes of CCPs per year.

Barriers to entry shall be further discussed in Section 5.

Markets for fly ash presently comprise of:

- Partial replacement of cement in concrete and concrete products;
- Flow-able fill projects including filling of out-dated sewer pipes and underground tanks as a substitute to excavation for replacement;
- Structural fills and embankments;
- Soil stabilisation for bearing capacity enhancements;
- Solidification and drying of non-toxic wastes for delivery to approved land fill sites;
- Agriculture and horticulture – soil amendment, fertilisers, zeolites;
- Manufactured products;
- Biochar;
- Others.

The main proponent of bottom ash marketing is the construction industry. The variations in bottom ash product specifications are evaluated with industry requirements to most successfully market the product. Bottom ash product is chiefly marketed for:

- Class 1A back fill;
- Biochar;
- Pipe bedding and drainage medium;
- Road-base application;
- Light aggregate for:
 - ... Light-weight concrete block;
 - ... Precast concrete products;
 - ... Light-weight concrete mix;
 - ... Construction fill material;
 - ... Traction control material;

... Light-weight flow-able fill mixtures.

Blast furnace slag is similar in physical properties to gasifier slag. The applications for blast furnace slag include:

- Aggregates
 - ... Concrete products such as blocks, bricks, roof tiles, etc
 - ... Concrete
 - ... Road base
 - ... Fill
 - ... Bitumen
- Cement kiln feed
- Cement mill additive
- Abrasives
- Soil conditioning
- Potential geo-polymer applications

Gasifier slag utilisation is currently not a widely applicable field, particularly in Australia. However, coal gasification generates solid waste materials in relatively large quantities. For example, a 100MW power plant based on IGCC technology using 1,000tons of 10% coal ash coal per day may generate over 110 tons/day of solid waste or slag (Choudhry, 1992).

The physical and chemical properties of coal gasification slags were found by Choudhry & Hadley (1992) to be related to the composition of the coal feestock, the method of recovering the molten ash from the gasifier, and the proportion of devolatilised carbon particles discharged with the slag. The rapid water quench method of cooling the molten slag inhibits recrystallisation and results in the formation of a granular, amorphous material. Some of the differences that were found were characterised by the specific design and operating conditions prevailing in the gasifiers. To generalise, slag generated by IGCC units is nominally in the 5x0.3 mm size range. This size range falls distinctly in the classification for fine aggregates used in cement concrete and asphalt concrete. The elemental composition is dependent on the feed coal; coal ashes are mostly comprised of silica, alumina, calcium and iron; slag fluxing agents attribute to the elemental composition also, they can result in an enrichment of calcium in the slag.

Selection of applications to utilise gasification slag take into account competition with convential materials. This consideration is both location and industry specific. In the USA, there is a much more pronounced history of gasification slag utilisation than in Australia. Here there is a precedent for standardisation of gasification slag utilisation in the cement industry with ASTM C 989-87a, which was adopted for utilisation of ground blast furnace slag as cement.

Choudhry and Hadley, (1992) investigated selection of the specific utilisation concepts and where guided by the following critiera:

- Similarity between the properties of slag and those of the material it replaces;

- Achievement of comparable final products meeting the necessary functional requirements.

Based on these criteria they devised the following list of utilisation concepts:

- Agriculture:
 - ... Soil conditioning;
 - ... Lime substitute;
 - ... Low analysis fertiliser;
 - ... Carrier for insecticides.
- Industrial material:
 - ... Abrasive grit;
 - ... Catalyst and adsorbent;
 - ... Roofing granules;
 - ... Industrial filler;
 - ... Mineral (slag) wool production;
 - ... Filter media.
- Cement and concrete:
 - ... Concrete aggregate;
 - ... Mortar/grouting material;
 - ... Pozzolanic admixture;
 - ... Raw material for Portland cement production;
 - ... Masonry unit production.
- Road and maintenance production:
 - ... Fine aggregate for bituminous pavement;
 - ... Base aggregate;
 - ... Sub-base aggregate;
 - ... Seal-coat aggregate.
- Landfill and soil stabilisation:
 - ... Soil conditioner to improve stability;
 - ... Structural fill;
 - ... Embankment material.
- Resource recovery: source of carbon, magnetite, iron, aluminium and other metals;
- Synthetic aggregate:
 - ... Lightweight construction aggregate;
 - ... Landscaping material;
 - ... Sand substitute.

In the USA, gasification slag has been determined to be an environmentally nonhazardous material. The report by Choudry & Hadley (1992) concluded that production of slag based lightweight aggregate holds strong prospects as saleable and economically viable product.

The properties of blast furnace slag are compared to fly ash, bottom ash and coal ash in Table 3.2. The glass content is important as a higher value gives blast furnace slag its self-cementing properties. This self-cementing property allows slag to accommodate various activators to enhance cementing action. The French road authority, SETRA has developed a

group of slag pavement types called ‘grave laitier’, or in English, ‘gravel slag’, using granulated slag as a binder with hydrated lime as an activator. This indicated the strong effect of this glass content property. Another promising attribute of slag is its purported resistance to sulphatic attack. Blast furnace slag shows this sodium sulphate resistance, but further testing needs to be undertaken with coal slag to ensure a similar property exists. The ratio comparisons shown in Table 3.2 show that even though the bulk gasifier slag is somewhat closer to blast furnace slag than bottom ash and fly ash, there is still a discrepancy between them.

Table 3.2: Composition Comparison for Boiler Ashes, Coal Ash, and Blast Furnace Slag

Compound	Blast Furnace Slag (%)	Bulk Gasifier Slag (%)	Furnace Bottom Ash (%)	Boiler Fly Ash (%)
SiO ₂	27-38	40-55	45-70	38-62
CaO	34-43	1-20	0.4-17	1-10
Al ₂ O ₃	7-13	12-25	15-30	20-40
MgO	7-15	1-6	1-6	0.9-4
Fe ₂ O ₃	0.2-1.6	9-15	2-15	6-16
Glass content	89-99			
Ratios				
(CaO+MgO)/SiO ₂	1.52-1.53	0.05-0.47	0.03-0.11	0.05-0.18
(CaO+MgO+Al ₂ O ₃)/SiO ₂	1.78-1.87	0.35-0.93	0.36-0.54	0.58-0.82
K ₂ O	0.31-0.72	0.1-1.2	0.1-0.4	1.1
Na ₂ O	0.20-0.45	0.2-1.3	0.5-2	0.8

3.2 FURNACE BOTTOM ASH UTILISATION

Furnace bottom ash is less widely utilised than fly ash. Part of the logic behind this statistic is the smaller proportion that the bottom ash represents of total boiler ash production, and thus the greater relative cost in handling and management of ash utilisation programs.

Bottom ash is typically grey to black in colour with angular particles and a very porous surface texture. This ash is predominately sand sized with about 50-90% passing 4.75mm, 10-60% passing 0.42mm and 0-10% passing a 0.075mm sieve. Top size typically ranges from 19 to 38.1mm (EPA, 2000).

Nonetheless, there is a growing interest in bottom ash for brick manufacture and other applications. For example, Gladstone Power Station bottom ash is undergoing utilisation programs with Adbin Masonry for application in non-structural bricks (Danby, 2011).

Bottom ash is an agglomeration of ash particles that are too heavy to carry over into the flue gas path. Typically, it is angular and porous in structure. This makes it most applicable for lightweight applications as opposed to gasifier slag, which is dense. It’s primary applications are as an aggregate, a feedstock for cement manufacturing, as a component in road or sub

bases, in construction applications in lieu of other constituents such as sand or gravel, for snow and ice control in overseas applications and in agriculture (Wearing, 2004).

In 2011, the undertaking between Adbin Masonry and Gladstone Power Station for the utilisation of their bottom ash in brick manufacture was in progress.

Adbin Masonry initiated the work due to the favourable cementitious properties of the Gladstone ash. Trial blocks have been manufactured and these blocks have been shown to meet marketability standards as held by Adbin Masonry and were responsible for these trials.

Work is ongoing and the proximity of Gladstone Power Station to the brick manufacturing plant and to a ready market makes the project viable.

3.3 BOILER FLY ASH UTILISATION

3.3.1 Uses

The chemical and physical properties of fly ash determine its suitability for various applications. For example, the ash at Gladstone Power Station is highly sought after for cementitious products, whereas that from Tarong Power Station is not (Shipperley, 2011). Selection for cement production is also effected by Australian Standards (Standards Australia, 1999).

Current and potential uses for fly ash include (Electric Power Research Institute, 1998):

- Cement and cement products;
- Manufactured products;
- Flowable Fill;
- Waste stabilisation;
- Agriculture and horticulture (soil amendment, fertilisers, zeolites);
- Structural fills and embankments;
- Others.

Application in cementitious products represent the largest portion of fly ash utilisation (CRC for Coal in Sustainable Development, 2007). Most scenarios of fly ash utilisation involve long term contracts with companies such as Cement Australia. Utilisation in cement is advantageous due to its high silica and alumina content. The feed material needs to be fine for this to be facilitated; slag material would require grinding.

Fly ash in concrete is post cement production and is part of the admixture. Fly ash is a pozzolanic addition and thus, is not inert. Other additions are blast furnace slag, silica fume and filler aggregates. Fly ash utilisation in this regard is well documented and is governed by a range of existing standards (Standards Australia, 1999).

Flowable fill is a backfill material which when mixed and deposited is fluid-like in behaviour and when in place gains sufficient strength at an early stage to determine later settlement. When a flowable fill is set it is similar in strength and physical properties to soil. A flowable

fill needs to be self leveling –flowable fills from fly ash may be manufactured from mixtures of Class C and Class F fly ash or from mixtures of other fly ash or bottom ash with either cement or lime. Application as a backfill material has been subject to detail examination by ACARP (2001). This study deemed it acceptable, although cost was considered a limiting factor.

There is a large body of literature relevant to the utilisation of fly ash for agricultural applications. The relevant properties of fly ash include (CRC for Coal in Sustainable Development, 2007):

- Readily available in large quantities;
- Often has a high pH for neutralisation of acidic soils;
- High trace element content;
- Ability to retain more water than most soils;
- A loosening effect when mixed with tight and heavily textured soils.

The issue in this arena is application and dosage. Some trace elements are particularly high and in excessive dosages can be deleterious.

As a structural fill, coal ash replaces natural aggregates. There is less governance in this field than that for cementitious products. It is, however, applied significantly in the USA and Europe,.

Hot rolled asphalt is another application where fly ash replaces the limestone dust. Fly ash has shown to be worked at much lower temperatures than conventional material, required less energy in preparation and had a lower bulk density and performed well in service (Barnes, 2004).

3.3.2 Case Study

Use of fly ash at Premier Mine in Collie Western Australia and works carried out for Wesfarmers Coal Ltd was reviewed. The consulting engineers, van der Meer & Associates and the contractor, Cardinal Contractors Pty Ltd were responsible for the review into the applicability of the use of the ash. A market for pavement material was realised and subsequent work was undertaken.

A trial pavement was constructed with fly ash from Muja Power station fly ash silos with addition of cement through a pugmill (Stewart, 1999). This pavement was constructed in a highly trafficked area and, following curing, was subjected to destructive testing using a Komatsu D355 Bulldozer. The advantages provided by the use of the Muja Power station fly ash and cement addition into pavement manufacture included:

- Full depth stabilisation of the pavement;
- Volumetric stability of the pavement due to lower permeability;
- Increase in compressive strength;
- Moisture stability of the pavement due to lower permeability;
- Workability of the material for placement due to the hydration process;
- Capital cost savings (including those on both cement and gravel);

- Potential maintenance cost savings.

Design detail of the pavements varied depending on the ultimate design traffic for various areas.

The pugmill was modified by the addition of a dedicated fly ash silo with screw feeder. Fly ash was transported to the silo by bulk tanker. The extreme dryness of the fly ash meant that water supply needed to be increased. The final design consisted of a fly ash content ranging from 4 to 6%.

3.4 UTILISATION OF IRON AND STEEL SLAG

3.4.1 Uses

Granulated blast furnace slag (GBFS) may be utilised without additional processing as construction sand, soil/pavement stabilising media or grit-blasting material. (Australasian Slag Association, 2011) Typical uses for GBFS are:

- As a general purposes construction sand in civil engineering applications and in various cementitious applications;
- As an ideal select fill behind reinforced earth wall construction. Within a relatively short time, the pozzolanic properties of granulate cause it to set and form a solid block;
- In glass manufacture as a source of alumina and silica;
- As a stabilising agent in road construction; there have also been examples where only granulate has been used in pavement material. Pavements now exist where granulate has been used in conjunction with steel slag to form very heavy-duty pavements;
- As a grit-blasting medium: granulate is particularly suitable on soft metals such as aluminium where a light etch is required.

3.4.2 Iron and Steel Slag Case Study

In Adelaide Brighton's Angaston cement plant in South Australia, a diminishing supply of Birdwood clay prompted an endeavour to locate an alternative raw material for its Brightonlite cement.

First, an action plan was developed and appropriate government approvals gained. Thereafter, Angaston began conducting blast furnace slag trials. Results found that the slag was an ideal alternative to Birdwood clay in the production of Brightonlite clinker (Department of Industry Tourism and Resources, 2006).

The calcium, silica and alumina in blast furnace slag all have had CO₂ driven off. This results in a net reduction in emissions of CO₂ in the kiln. Additionally, the calcined calcium in the slag replaces limestone in the raw mix, which conserves a non-renewable resource.

3.5 USE OF GASIFIER DERIVED SLAG IN USA

3.5.1 Applications

Gasifier derived coal slag can be utilised for the following applications (Schumacher, 2011):

- Cement kiln feed;
- Cement mill additive;
- Abrasives;
- Soil conditioning;
- Aggregates:
 - ... Concrete products (blocks, roof tiles, etc);
 - ... Concrete;
 - ... Road base;
 - ... Fill;
 - ... Bitumen.

3.5.2 Case Study

As there are no IGCC power stations operational in Australia, investigation was undertaken into gasification plants overseas. There are two IGCC plants in operation in the United States. Tampa Electric IGCC Power Plant located in Polk County, Florida produces bottom slag and sulphur in acid form; whereas the Wabash station in Indiana produces bottom slag and sulphur in elemental sulphur form. The Wabash River IGCC plant in Indiana undertook an evaluation of the production fire bricks from the coal slag generated at that plant (Lu-Ming Chen, 2009).

Slag from the Wabash River IGCC plant and processed clay and shale, required in the manufacture of conventional fired bricks, comprised the raw materials for the fire brick manufacture. The particles in the as received slag were screened into four size fractions; greater than 8 mesh, -8 +60 mesh, -60 +100 mesh and -100 mesh. This yielded a distribution of 30.2%, 63.8%, 3.6% and 2.4% respectively. This material was reduced until all material passed through the 8 mesh screen. The resulting distribution was 82% between 8 and 60; 7.3% between 60 and 100 and 11.2% below 100 mesh (Lu-Ming Chen, 2009).

Brick production was via a mould pressed methodology. The three formulations were:

- No.1 Clay : Shale – 14%:86%;
- No.2 Clay : Shale : Slag – 14%:76%:10%;
- No.3 Clay : Shale : Slag – 14%:66%:20%.

The firing program was undertaken at the bench-scale kiln at Illinois State Geological Survey. The maximum firing temperature was 1,955°F. Evaluation of the bricks was undertaken by measurement of total shrinkage, colour, appearance, texture, marketability (based on brick company specifications), cold water absorption (ASTM C62), boiling water absorption (ASTM C62) and compressive strength.

The bricks were found to meet all relevant grades and standards, and had less total shrinkage. The bricks were found to be of high quality and marketable.

3.6 ECONOMICS OF ASH UTILISATION

Presently, ash utilisation is mainly demand driven. Ash generators rarely create or research potential markets.

For cementitious application, the ideal scenario is 1:1 replacement of cement by fly ash. This would give the fly ash a much higher associated value than if the proportion of replacement is below 1:1. At present, the actual value is less than the cost of cement production (Heeley, 2003).

As discussed in Section 5, transport is the primary utilisation issue. This is a cost generally borne by the party wishing to utilise the ash. Another important consideration is the avoided cost of disposal; this is a benefit accrued to the producer. Subsequent cost considerations include product processing costs, which are also borne by the ash user, not by the utility.

The economics of ash utilisation are positive if the avoided cost of disposal (C_a) plus the cost of product recovery and processing (C_r) and transport (C_t) are less than the value of the product in the hands of the end user (V_u). This is mathematically expressed as:

$$C_a + C_r + C_t < V_u$$

The avoided costs and end value can be difficult to monetise due to the subjective factors that are integral to the result. The issue with transport in Australia is clearly the long haulage distances involved. However, ash utilisation is becoming of greater interest in Australia due to the nearing end of life of many of the ash storage facilities that were installed at power plant construction stages. This is indicative of the age of plants in Australia. It results in a more favourable avoided cost, which makes utilisation more viable. Most power stations in Australia continue to operate wet slurry disposal systems. These have very low costs per tonne of ash; however, as plants near the end of storage capacity they can first raise dam walls at a typical cost of \$2 to \$3/t; then beyond that there is a need to implement entirely new storage disposal systems which introduces significant capital expenditure.

Without any outside drivers, the avoided cost factor is only \$3 to \$4/t. However, this can quickly rise where drivers such as end of storage facility capacity are relevant. Bear in mind also that ash storage dams incur costs until they are fully shut down and rehabilitated; this cost therefore continues even after new ash storage facilities or utilisation avenues are implemented. In this cost are considerations such as water quality monitoring, dust and leachate management, modifying regimes as well as others. This can be up to another \$2/t for a theoretical 1,000MW facility (Heeley, 2003). Some stations such as Mt Piper in NSW incur much greater costs. This is due to the truck based operation implemented.

The avoided cost of disposal in Australia is currently much lower than that experienced in some countries overseas. This is largely due to fees applied to disposal of ash rather than its utilisation. These charges can be as much as US\$50 to US\$60/t in some US states and between €10 and €60/t in Europe.

In Australia, it is feasible that a fee of \$18 to \$20/t could be introduced for ash disposal (Heeley, 2003). This would be an incentive scheme to encourage ash utilisation.

The bureau of Industry Economics in its report (BRE 45, 1992) indicated that the structure of the cement industry and particularly the vertical integration of quarries, cement

manufacturers and concrete suppliers were factors which limit the use of fly ash and slag in concrete. Part of the cause for this is suggested to be transportation costs, capital equipment costs and slow growing, highly inelastic demand. These factors not only limit price competition, but also limit motivation on behalf of cement and concrete industries to reduce their cement consumption and replace it with another product. If capital equipment that has already been purchased is going to be underutilised, that is an efficiency shortfall in terms of investment value maximisation.

Typical sale price of fly ash in metropolitan areas is between \$60 and \$80/t. Compared with cement at \$150/t there is still a significant business incentive. The ADAA shows that cementitious application of power station ash has increased from around 10% to around 20% in just over 20 years (ADAA, 2008).

Other factors influencing uptake of ash utilisation and improvement of ash utilisation economics includes the introduction of CO₂ reduction incentives as cement manufacture is a highly CO₂ intensive process; and also the need to update Australian standards to allow for a higher proportion fly ash concrete to be applied across construction applications. Currently only the standard concrete mix is permitted replacement of up to 40% fly ash. Specialised mixes allow for no such considerations.

In bulk fill considerations, fly ash or bottom ash is only valued at around \$15/t for the end user. This indicates that very efficient processes must be implemented to make such an endeavour financially viable. Small niche markets, such as free draining fill for retaining walls are more viable, but markets are small and prices are still only in the range of \$20 to \$30/t (Heeley, 2003).

Some more promising figures arise from soil improvement projects. Such projects have been undertaken in Western Australia and have successfully reduced water consumption by around 75% with a dosing of fly ash of about 100t/ha (about \$4,000/ha). The water retention resulted in a saving greater than the cost of implementation after just one year and the effects spread beyond water retention through to added available nutrients in the soil through fly ash application (Heeley, 2003).

4 LEGISLATION AND REGULATION OVERVIEW

4.1 INTRODUCTION

In the vast majority of countries, ash derived from coal-fired power generators is not regarded as a hazardous waste. It is however, deemed to be a waste as the larger portion of ash generated is discarded to landfill or dams, and is thus treated as a waste material.

Ansley et al (2003) stated that there are only few instances where legislation specifically addresses the question of ash disposal and was deemed to be a waste in a number of legislative documents. This determination created barriers for better utilisation, but is undergoing advancements. Regulations have been developed to address the use of CCPs in agricultural and industrial applications both in New South Wales and Queensland and recent requirements written into approvals for ash disposal redevelopments for improvement to the amount of ash being reused (EPA, 2000), (Nelson, 2008), (Heidrich, 2008).

The descriptor CCP (coal combustion products) is commonly used by industry bodies to avoid the term “waste”. However, government regulations do specify ash as a waste rather than a product. Regulations governing the disposal of waste are outlined in the following sections.

4.2 INTERNATIONAL AGREEMENTS

International agreements exist that govern the disposal of coal ash. These are covered, to a large degree, by the Basel Convention. The two primary administrative bodies for this are the United Nations (UN) and the Council of the Organisation for Economic Co-operation and Development (OECD).

The Basel Convention on the control of trans-boundary movements of hazardous wastes and their disposal was adopted by the UN in 1989. (Riley, 2005) The text of the Basel convention 1989 is available at: <http://www.basel.int/text/con-e.pdf>. Annex I of the document designates the categories of wastes to be controlled. This incorporates wastes with the following constituents:

- Beryllium;
- Hexavalent chromium;
- Copper;
- Zinc;
- Arsenic;
- Selenium;
- Cadmium;
- Antimony;
- Tellurium;
- Mercury;
- Thallium;
- Lead.

All of these compounds can be found in coal ash. Typical ranges in the flyashes of Australian bituminous coals shown in Table 4.1 (Riley, 2005).

Table 4.1: Typical Ranges of Compounds in Fly Ash from Australian Coals

Compound	Typical range in Australian Fly Ash (mg/kg)
Beryllium	4-24
Chromium	18-130
Hexavalent chromium	<0.2-13
Copper	28-99
Zinc	70-290
Arsenic	5-22
Selenium	2.5
Cadmium	0.2-1.4
Antimony	1-4
Tellurium	<1
Mercury	0.02-0.24
Thallium	<1
Lead	50-80

Annex VIII in List A of ‘wastes characterised as hazardous’, stipulates that a waste is deemed hazardous if; “A2600 Coal-fired power plant fly-ash containing Annex I substances in concentrations sufficient to exhibit Annex III characteristics.” Annex III characteristics are as follows:

- a) 9 H12 Ecotoxic – Substances or wastes which if released present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems;
- b) 9 H13 Capable by any means, after disposal, of yielding another material, e.g. leachate, which possesses any of the characteristics listed above.

In Annex IX, (effective as of 20 November 2003) is List B; “Wastes contained in the Annex will not be wastes covered by Article 1, paragraph 1 (a) of this Convention unless they contain Annex I material to an extent causing them to exhibit an Annex III characteristic”, where Article 1, paragraph 1(a) is as follows:

“ ...

1. The following wastes that are subject to transboundary movement shall be “hazardous wastes” for the purposes of this Convention:

- (a) Wastes that belong to any category contained in Annex I, unless they do not possess any of the characteristics contained in Annex III;

...”

In this list is “B2050 Coal-fired power plant fly-ash not included on list A”.

Therefore, it can be seen that in accordance to the Basel Convention, fly ash is indeed not a hazardous waste unless it or products derived from it contain a toxic substance or substances at concentrations which exhibit a “hazardous characteristic” (Basel Convention, 1992).

4.3 NATIONAL

The Australian waste and subsequent coal ash disposal legislation is most relevantly based upon the Hazardous Waste Act of 1989, which is the implementation of the Basel Convention (Aynsley, 2003).

Within this act, those UN Hazardous Characteristics that are applicable to coal ash are:

- 9H12 Ecotoxic – Substances or wastes which if released present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems;
- 9H13 Capable by any means, after disposal, of yielding another material, e.g. leachate, which possesses any of the characteristics listed above;
- H6.1 Poisonous (Acute) – Substances or wastes liable either to cause death or serious injury or to harm health if swallowed or inhaled or by skin contact;
- 9H11 Toxic (Delayed or chronic) – Substances or wastes which, if they are inhaled or ingested or if they penetrate the skin, may involve delayed or chronic effects, including carcinogenicity.

It is deemed unlikely that typical coal ashes would present these concerns (HBM Group Pty Ltd, 2010).

Additionally, the Environmental Protection Authority (EPA) has stipulated a Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption under Part 6, Clause 51 and 51A. This is the coal ash exemption 2011 effective as at 14 June 2011. These clauses authorises (Environment Protection Authority, 2011):

- The EPA to grant an exemption in relation to any matter or thing including an activity or class of activities;
- The EPA to exempt a person from any of the following provisions in relation to an activity or class of activities relating to certain waste that is to be land applied or used as a fuel:
 - ... The provisions of sections 47 to 49 and 88 of the *Protection of the Environment Operations Act 1997* (the Act);
 - ... The provisions of Schedule 1 to the Act, either in total or as they apply to a particular activity;
 - ... The provisions of Part 3 and clauses 45 and 47 of the Regulation.

In the notice of exemption (effective as at 14 June 2011):

- The responsible person listed in Column 1 of Table 4.2 is exempt from the provisions/s listed in Column 2 of that table but only in relation to activities involving the relevant waste and only where the responsible persons does comply with the conditions as set out in Column 3. This notice does not exempt the responsible person from the

provisions as described in Column 2 where the relevant waste is received at premises that are, despite this exemption, required to be licensed for waste disposal activities under the provisions of the Act;

- Where a responsible person complies with the conditions of this Notice of Exemption, the activity referred to in Schedule 1 from which that person is exempt is taken to be a non-scheduled activity for the purposes of the Act.

Table 4.2: Table 1 from Coal Ash Exemption 2011

Column 1	Column 2	Column 3
Responsible person	Provisions from which the responsible person is exempt	Conditions to be met by the responsible person
Generator	section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation	all requirements specified in section 7 and 8
Processor	section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation	all requirements specified in section 7 and 9
Consumer	section 48 of the Act in respect of clauses 39 and 42 of Schedule 1 to the Act Part 3 of the Regulation section 88 of the Act clause 47 of the Regulation	all requirements specified in section 7 and 10

General conditions of the exemption as per the Notice of Exemption are as follows:

- The chemical concentration of the coal ash as listed in Column 1 of Table 4.3 must not exceed the following:
 - ... The absolute maximum concentration or other value listed in Column 4 of Table 4.3;
 - ... For characterisation or one-off tests, the maximum average (as based upon the arithmetic mean) concentration or other value listed in Column 2 of Table 4.3;
 - ... For routine tests, the maximum average (as based upon the arithmetic mean) concentration or other value listed in Column 3 of Table 4.3.
- The coal ash can only be applied to land as an engineered fill, stabiliser, filter or drainage material or as a sand substitute as follows:
 - ... Pipe bedding material;
 - ... Selected backfill adjacent to structures;
 - ... Composite filler in asphalt pavements;
 - ... Road pavement, base and sub-base structures;
 - ... Rigid and composite pavement structures;
 - ... Select layers which act as working platforms at the top of earthworks;
 - ... Fill for reinforced soil structures (including geo-grid applications).
- The coal can only be applied to land consistent with section 7.2 where:
 - ... It complies with a relevant specification or Australian Standard or supply agreement/s;
 - ... Planning or development consent that has specifically considered the use of coal ash has been granted for the project.

- The coal ash can be applied to land consistent with section 7.2 when blended with other exempted materials, provided the blended materials have been validated as compliant with the conditions of each individual exemption, for the use specified in each exemption.

Generator responsibilities for the exemption to apply include: (Environment Protection Authority, 2011)

- Sampling must be undertaken in accordance with Australian Standard 1141 Methods for sampling and testing aggregates (or equivalent); this includes requirement of sampling and information pertaining to sample storage and preparation to be detailed in a written sampling plan;
- Where the coal ash is generated as part of a continuous process, the generator must undertake characterisation and routine sampling according to the requirements listed in Column 1 and Column 2 of Table 4.4, for the range of chemicals and other attributes as listed in Column 1 of Table 4.3;
- Where the coal ash is not generated as part of a continuous process, the generator may undertake a one off sampling of a batch, truckload or stockpile of coal ash according to the requirements listed in Column 3 of Table 4.4, for the range of chemicals and other attributes listed in Column 1 of Table 4.3;
- Where there is a change in inputs that is likely to affect the properties in the coal ash, characterisation shall be repeated; characterisation samples can be used for routine testing and subsequent calculations;
- Generators shall keep a written record of all characterisation, routine and/or one off test results for a period of five years;
- Records of the quantity and proposed use of coal ash supplied to the processor or consumer and the processors or consumer's name and address shall be kept for a period of five years;
- The generator of coal ash shall provide a written statement of compliance to the processor or consumer with each transaction to certify that the coal ash complies with the relevant conditions of this exemption;
- The generator of coal ash must make information on the latest characterisation and routine test results available to the processor or the consumer;
- The generator of the coal ash must use due diligence to ensure that the relevant waste is utilised in applications that are consistent with the conditions of this exemption.

Processor responsibilities for the exemption to apply include the following:

- Records of the quantity and proposed use of coal ash supplied to the consumer and the consumer's name and address must be kept for a period of five years;
- Records of the quantity of ash received by the processor from the generator and the generators name and address must be kept for a period of five years;
- The processor of coal ash must provide a written statement of compliance to the consumer with each transaction to certify that the coal ash complies with the relevant conditions as stipulated by this exemption;
- The processor of coal ash shall make information on the latest characterisation and routine test results available to the consumer;

- The processor of coal ash must use due diligence to ensure that the relevant waste is utilised in applications that are fully consistent with the conditions as stipulated within this exemption.

Consumer responsibilities for this exemption to be applicable include:

- Records of the quantity and use of the coal ash received by the consumer and the suppliers' name and address shall be kept for a period of five years;
- The coal ash shall not be applied in or beneath water including ground water;
- The consumer should note that regardless of having an exemption, the use of coal ash remains subject to ALL other relevant environmental regulations within the Act and Regulations, including but not limited to land pollution (s142A) and water pollution (s120);
- The consumer shall land apply the relevant waste within a reasonable period of time.

The chemical and other material property requirements as per this exemption are such that the attributes in Column 1 of Table 4.3 comply with those stipulations from the other Columns of Table 4.3. While limits are not included for electrical conductivity this must be tested and results recorded for each sample.

Table 4.3: Table 2 from the Coal Ash Exemption 2011

Column 1	Column 2	Column 3	Column 4	Column 5
Chemicals and other attributes	Maximum average concentration for characterisation (mg/kg 'dry weight' unless otherwise specified)	Maximum average concentration for routine testing (mg/kg 'dry weight' unless otherwise specified)	Absolute maximum concentration (mg/kg 'dry weight' unless otherwise specified)	Test method specified within Section
1. Mercury	0.5	Not required	1	13.1
2. Cadmium	0.5	0.5	1	13.2
3. Lead	25	25	50	13.2
4. Arsenic	10	Not required	20	13.2
5. Boron	75	Not required	150	13.2
6. Chromium (total)	25	25	50	13.2
7. Copper	20	Not required	40	13.2
8. Molybdenum	10	Not required	20	13.2
9. Nickel	25	25	50	13.2
10. Selenium	10	10	20	13.2
11. Zinc	35	35	70	13.2
12. Electrical Conductivity	NA	NA	NA	13.3
13. pH*	7 to 12.5	7 to 12.5	6 to 13	13.3

*Note: The ranges given for pH are for the minimum and maximum acceptable pH values in the coal ash.

This Notice of Exemption only applies to coal ash sampled according to the requirements in Table 4.4.

Table 4.4: Table 3 from the Coal Ash Exemption 2011

Column 1	Column 2	Column 3
Characterisation sampling frequency	Routine sampling frequency	Once-off sampling frequency
20 composite samples, by taking 1 composite sample from a different batch, truckload or stockpile. This must be repeated every 2 years.	Either 5 composite samples per 10,000 tonnes or 5 composite samples per 6 months.	10 composite samples per 4,000 tonnes e.g. discrete once-off delivery or ship load.

Test methods shall be undertaken by analytical laboratories accredited by the National Association of Testing Authorities, or equivalent. All chemicals and other attributes listed in Column 1 of Table 4.3 shall be measured in accordance with the methods specified:

- Test method for measuring mercury concentration in coal ash
 - ... Particle size reduction and sample splitting could be required;
 - ... Analysis by USEPA SW-846 Method 7471B Mercury in solid or semisolid waste, or an equivalent analytical method with a detection limit less than 20% of the stated absolute maximum concentration in Table 4.3, Column 4;
 - ... Report as mg/kg dry weight.
- Test methods for measuring chemicals 2-11 in coal ash:
 - ... Particle size reduction and size splitting could be required;
 - ... Sample preparation by digestion using USEPA SW-846 Method 3051A microwave assisted acid digestion of sediments, sludges, soils and oils;
 - ... Analysis using USEPA SW-846 Method 6010C Inductively coupled plasma – atomic emission spectrometry, or equivalent analytical method with a detection limit of less than 10% of the stated absolute maximum concentration in Table 4.3, Column 4;
 - ... Report as mg/kg dry weight.
- Test methods for measuring the electrical conductivity and pH in coal ash:
 - ... Sample preparation by mixing 1 part coal ash with 5 parts distilled water;
 - ... Analysis using Method 103 (pH) and 104 (Electrical Conductivity). In Schedule B (3): Guideline on Laboratory Analysis of Potentially Contaminated Soils, National Environment Protection (Assessment of Site Contamination) Measure 1999 (or an equivalent analytical method);
 - ... Report electrical conductivity in deciSiemens per metre (dS/m).

4.4 LEGISLATION AND REGULATIONS ON BLAST FURNACE SLAG UTILISATION

Australian Standard 3582.2-2001 identifies the primary regulations imposed upon blast furnace slag utilisation.

Sampling procedures shall be taken in accordance with:

- AS1199 Sampling procedures and tables for inspection by attributes

- AS1399 Guide to AS1199
- AS1141.3.1 – Methods for Sampling and Testing Aggregates 1996 (Method 3.1 – Sampling Aggregates: Section 6.9 – Sampling from Stockpiles)

Blast furnace slag also follows the Waste Legislation as per details given above in the National and the State Specific Sections.

As there currently exists no Australian or state specific gasifier slag legislation, the blast furnace slag legislation is a sound guide for approval criteria. Table (2) on page 5 of Appendix A provides a valuable acceptance model which offers upper limit advice on chemical and other attributes. Blast furnace slag legislation is a more accurate guide than fly and bottom ash due to its similarities in physical attributes and leach-ability. These acceptance criteria are useful in estimating approval from the relevant environmental protection authority.

Table 4.5 briefly evaluates the state specific legislation for blast furnace slag. Where detailed legislation exists, the acceptance criteria for each state is comparable.

Table 4.5: Blast Furnace Slag Legislation (www.asa-inc.org.au; 2012)

State	Regulatory Waste Status	Exemptions Status	Exemption Criteria	Transport Exemption	Legal Status
Victoria	Waste	Yes Project specific: Expires	Field Rule Not specified Subject to review 100xStd drinking water reg.	Yes Project Specific Expires: Fees Apply	Waste
New South Wales	Waste Licence requirements >20kts	Yes Project specific	See Error! Reference source not found. for detail (general, generator, processor and consumer specific exist	Yes Project Specific: Fees Apply	Waste
Queensland	Waste	Yes BRA Project and resource type specific	None Application specific No thresholds Case by Case	Yes Project Specific: Fees Apply	Waste Exemption after BRA granted
South Australia	Not defined Responsibility for determination rest with the generator	None Identified Case by Case	None	Yes Project Specific Expires Fees Apply	Unclear – Waste
Western Australia	Not defined Responsibility for determination rest with the generator	None Identified Case by Case	None	Yes Project Specific Expires Fees Apply	Unclear – Waste

4.5 AUSTRALIAN STATE SPECIFIC FOR COAL ASH

Each State may have nuances regarding the specifics of their legislation. The following sections outline state specific differences and additions or other

considerations to be adhered to above those outlined in the National Legislation Section 4.3. More details can be found in the reference given in these sections.

4.5.1 Queensland

In Queensland coal ash is listed in Schedule 7, Regulated Wastes and is covered by the exemption as outlined in Section 4.3.

4.5.2 New South Wales

In New South Wales coal ash falls under waste legislation. This is covered by the Protection of the Environment Operations Act, and therefore is covered by the exemption as outlined in detail in Section 4.3

4.5.3 Victoria

In Victoria coal ash was a prescribed waste under the Prescribed Waste Regulation, 1998. (HBM Group Pty Ltd, 2010) The Environment Protection (Industrial Waste Resource) Regulations 2009 have replaced both the Environment Protection (Prescribed Waste) Regulations 1998, and the Industrial Waste Management Policy (Prescribed Industrial Waste) 2000. The new Regulations came into effect on July 1 2009. Guidance to support these Regulations is provided in the Industrial Waste Resource Guidelines. These Resource Guidelines stipulate that of particular focus is the reduction of Category B PIWs with the intent of achieving the State government’s objective of eliminating its disposal to landfill by 2020 (Environmental Protection Authority - Victoria, 2011).

The Victorian EPA describes disposal as the least preferable option, as shown in Figure 4.1.

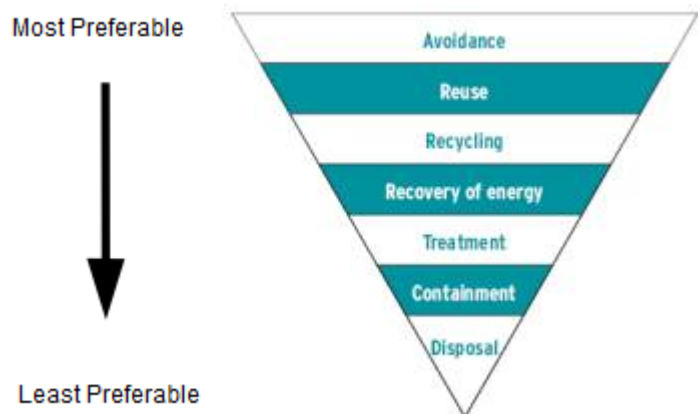


Figure 4.1: Waste Management Hierarchy

Although coal ash in Victoria still falls under the category of prescribed waste, disposal is arranged via appropriate leachate and other testing and acquisition of all appropriate approvals.

Exemption for secondary beneficial reuse can be authorised by the Victorian EPA:

- Of its own motion; or
- When a prescribed industrial waste producer or waste receiver has provided a notification of the reuse to the Victorian EPA;

...When in accordance with Part 5 of 'Environment Protection (Industrial Waste Resource) Regulations 2009 S.R. No. 77/2009'.

Establishing a secondary beneficial reuse is established when:

- A prescribed industrial waste producer or waste receiver has provided a notification of the reuse to the Authority in accordance with regulation 40; and
- The Authority has authorised the notification in accordance with regulation 41;
- And also when the Authority authorises a secondary beneficial reuse notification of its own motion within Part 5 of 'Environment Protection (Industrial Waste Resource) Regulations 2009 S.R. No. 77/2009';
- And may be limited to the types, classes or consignments of waste specified in the authorisation of notification by the Authority.

4.5.4 Western Australia

There is no specific legislation in Western Australia on the use and disposal of coal ash. As with all states the waste is covered by various environmental regulations. (HBM Group Pty Ltd, 2010) Reuse of waste is an item of interest in the Western Australian Government and is largely covered by the *Waste Avoidance and Resource Recovery Act 2007*. The objects of this Act are: (Waste Management Board, 2007)

- Promoting the most efficient use of resources including resource recovery and waste avoidance; and
- Reducing environmental harm, including pollution through waste; and
- The consideration of resource management options against the following hierarchy:
 - ... Avoidance of unnecessary resource consumption;
 - ... Resource recovery (including reuse, reprocessing, recycling and energy recovery)
 - ... Disposal.

4.5.5 South Australia

The EPA South Australia regulates the waste and resource recovery industry through the provisions of the *Environment Protection Act 1993* (the Act). In addition the EPA has specific powers in relation to conditions of approval for activities that require approval under the *Development Act 1993* (Environmental Protection Authority - South Australia, 2011).

Relevant sections of the Act include

Section 10 – Objects of the Act

These are to prevent, minimise or eliminate harm to the environment as far as possible.

Section 25 – General environmental duty

This section outlines the responsibilities of a person, whether or not licensed, when undertaking an activity that may pollute the environment, to take all reasonable and practicable measures to prevent or minimise environmental harm.

Section 36 – Requirement for licence

This section outlines the requirement for a person undertaking a prescribed activity of significant environmental impact to have an environmental authorisation

Sections 40 and 48 – Grant of licence and annual fee

These sections outline the requirement for the holder of an environmental authorisation to pay an authorisation fee (see the *Environment Protection Regulations 2009* for further information on this).

Section 113 – Waste depot levy

This section outlines details of those required to pay the waste depot levy and is linked to the *Environment Protection Regulations 2009* which details who must pay and the amount required.

Schedule 1

Schedule 1 lists activities of environmental significance under which a licence from the EPA is required for operation. The majority of these are listed under Activey 3, Waste Treatment and Disposal.

4.5.6 Northern Territory

The Crown Lands Act, 1931-1991 refer to permits for a lessee to use land and waters for the purpose of ash disposal ponds. (HBM Group Pty Ltd, 2010) Otherwise little specifically coal ash related legislation is available; coal ash follows the National Legislation and those relevant stipulations under the Northern Territory Government *Waste Management and Pollution Control Act*. (Natural Resources, Environment, The Arts and Sport - Northern Territory Government, 2007)

The Act covers several key points (Natural Resources, Environment, The Arts and Sport - Northern Territory Government, 2007) There is a duty to notify of incidents or threats to the environment; the notification must include:

- The incident;
- The place, date, and time;
- How the pollution may occur, is occurring or has occurred;
- Any attempts to deal with the situation or potential situation;
- Contact details of the notifier.

5 EXISTING BARRIERS

It is in both the community and the generators best interest to curtail ash flow to waste impoundments of all categories and to augment that which is directed towards productive streams (Aynsley, 2003). Unfortunately, there are existing constraints which make such augmentation difficult. These entail, but are not exclusive to:

- Extraction and transportation of ash to cementitious product users; this utilisation tends to be mostly applicable only where generators are in proximity to the plants utilising the material (Heeley, 2003);
- Market for use of material must be adequate and of feasible proximity;
- Lack of responsibility by coal producers for their product due to ash not being a core product (Heeley, 2003);
- Uncertainty of regulators on the environmental effects of ash on water in unbound applications (Ward, 2006);
- Competition between ash producers (Heeley, 2003);
- Vertical integration of the cement, concrete and quarrying industries (Heeley, 2003);
- Regulation on ash in non-bound applications such as fills and agriculture;
- Legislative disparities from state to state;
- Classification of ash as an industrial waste by some states;
- Unburned carbon;
- Pores within the slag surface;
- Colour, shape, size and friability of the slag;
- Alkalis present in ash comprising cementitious products can deteriorate the structural integrity of concrete products;
- Trace element content can exclude ash products from viability for some utilisation avenues;

The most commonly referenced consideration in terms of barriers to ash utilisation is transport in the context of cost. Transportation is neither difficult nor technologically challenging; however ash is fine and prone to dust, moisture considerations in transportation are fundamental in some applications and distances are often vast between the producer and the user; these factors all result in additional cost. The closer the producer and user are, the more viable the ash utilisation endeavour is likely to be.

There are typically two ways of transporting ash, these are wet and dry. The end application is the usual consideration which dictates which option is pursued. In most cementitious applications the ash is required in dry powder form. Alternately, in application of furnace ash for sand replacement in cement, some moisture is acceptable and this makes dust management in transportation far simpler.

Dry transport typically implies sealed pneumatic tankers or pipelines. Tankers are most flexible in application but they come at a substantial cost over standard trucks. Open tip trucks are standard, these come at a benchmark of approximately 10¢/t/km; add loading of \$3 to \$5/t (Heeley, 2003). This is the cheapest transportation option. If controlled moisture content is allowed it can reduce dust problems but adds a premium to the loading from \$3 to \$5/t to between \$5 and \$8/t. Fully dry transportation is far dearer with a cost in the

range of €15 to €25/t/km and a life cycle cost for loading in the order of \$3 to \$4/t (Heeley, 2003). The alternative, being pipelines, are economical only for short runs of less than 1 km or for extremely large volumes such as into old open cut mine works. For a 20 year project with a capacity of 1.5 mtpa this equates to less than \$3/t where the ash is being backfilled from the power station to the old mine pit.

5.1 FUTURE CONSIDERATIONS IN TERMS OF BARRIERS

The use of existing leaching tests has been subjected to extensive debate in the literature. The USEPA (United States Environmental Protection Agency) developed the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP has suffered criticism due to an overly broad application of the test (Kosson, 2002). Scott et al (Scott, 2005) reviewed leach methodologies from an Australian perspective and concluded that TCLP was limited in its usefulness as a regulatory tool in Australia.

This indicates that changes to the regulation of coal combustion products is likely and shall be liable to becoming more stringent in their application.

6 SUMMARY OF FINDINGS

The primary concerns addressed by this report are as follows:

- Best practice in the ash disposal industry;
- Best practice in the ash utilisation market;
- Transport and other constraints and barriers placed upon the ash utilisation market;
- The economics of ash utilisation is briefly addressed;
- Current and potential legislative and HSE impacts.

The objective of this report is to arrive at a broad overview of the ash utilisation industry and how it is likely to be imposed upon the potential IGCC slag market.

Currently, approximately two thirds of fly ash produced is disposed as waste. Of the quantity utilised the primary portion is utilised within the cementitious products market. In this arena, the value of the final product is relatively low and as such can easily be made unfeasible through transportation expenditure. The transport logistics and costs are increased if the volume of useable product is relatively low such as in smaller plants or plants where the quality of ash is not generally applicable to successful cementitious or other similar application. This relative cost is likely to become less of a problem if governing bodies impose levies upon ash storage, similar to many international bodies; currently the Netherlands taxes generators €65/t for disposal (Heeley, 2003).

Where there is a ready market in the vicinity to potential IGCC plant locations; IGCC slag is a viable by-product. This is more-so the case than with fly ash as the slag is bound and has reduced leachate concerns and also due to being larger, heavier and denser in physical properties it poses less of a concern with fugitive dust. Thus transport presents less of a logistical concern.

Ongoing concerns that could limit the acceptance of IGCC slag and the utilisation of IGCC slag are:

- Community acceptance of increased CCP utilisation in community products needs to be resolved for more widespread integration into engineering materials, agriculture and other potential fields;
- Generators must view ash as a product and not an inconvenience or waste material;
- Markets must be made aware of the potential utilisation and the benefits of the product;
- Legislation and standards must be introduced into the market such that end users are comfortable with the viability of the material in place of traditional materials;

Current companies related to the ash utilisation market are outlined in Figure 6.1.

These companies exemplify users of waste materials who could be contacted to arrange trials for gasifier slag utilisation projects. The gasifier slag waste could be directly incorporated into existing utilisation schemes.

Approvals can be acquired by application with the relevant environmental protection authorities.

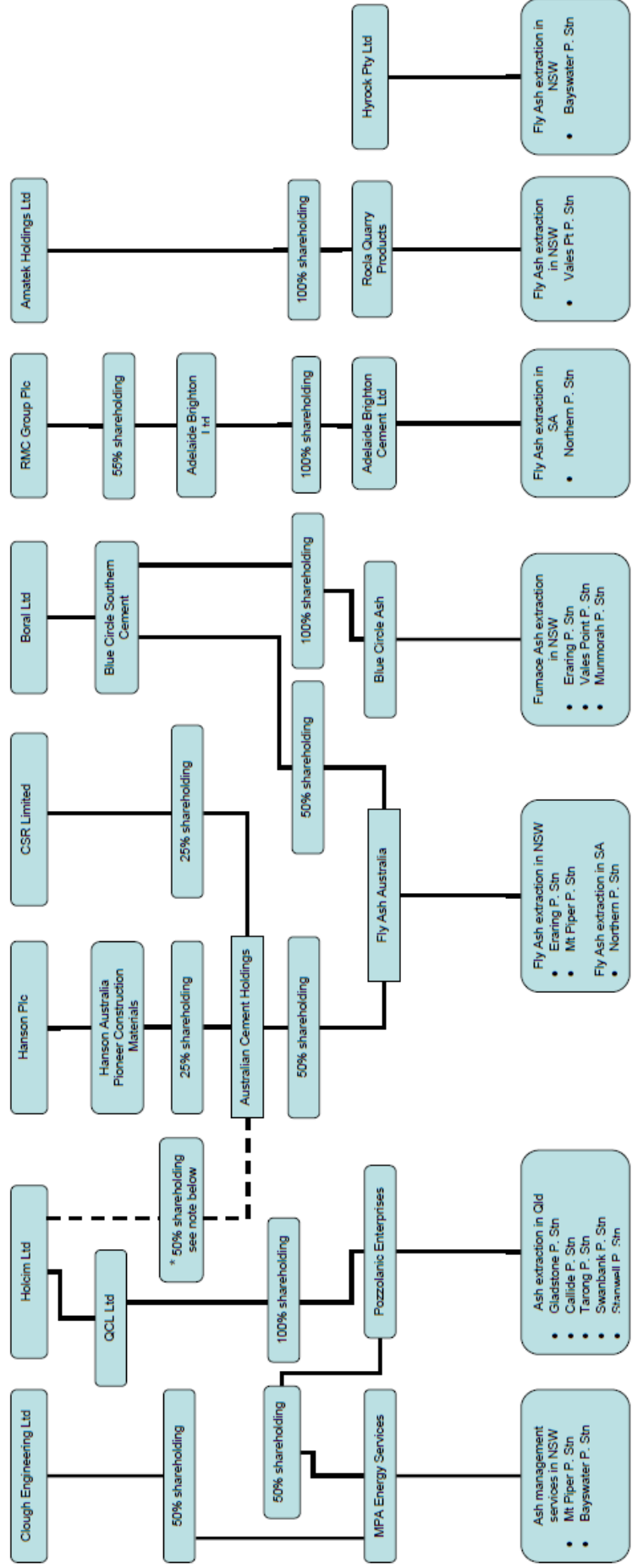


Figure 6.1: Ownership of companies associated with Ash Utilisation in Australia

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APPENDICES

APPENDIX A: BLAST FURNACE SLAG REGULATION 2010

Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption Under Part 6, Clause 51 and 51A

The blast furnace slag exemption 2010

Name

1. This exemption is to be known as 'The blast furnace slag exemption 2010'.

Commencement

2. This exemption commences on 27 December 2010.

Duration

3. This exemption is valid unless revoked by the Environment Protection Authority (EPA) by notice published in the Government Gazette. 'The blast furnace slag exemption 2010' which commenced on 5 March 2010, is revoked from 27 December 2010.

Legislation

4. Under the *Protection of the Environment Operations (Waste) Regulation 2005* (the Regulation):

- 4.1. Clause 51 (2) authorises the EPA to grant an exemption in relation to any matter or thing including an activity or class of activities, and
- 4.2. Clause 51A authorises the EPA to exempt a person from any of the following provisions in relation to an activity or class of activities relating to certain waste that is to be land applied or used as a fuel:
 - the provisions of sections 47 to 49 and 88 of the *Protection of the Environment Operations Act 1997* (the Act),
 - the provisions of Schedule 1 to the Act, either in total or as they apply to a particular activity, and
 - the provisions of Part 3 and clauses 45 and 47 of the Regulation.

Exemption

5. In this Notice of Exemption:

- 5.1. The responsible person listed in Column 1 of Table 1 is exempt from the provision/s listed in Column 2 of that table but only in relation to activities involving the relevant waste and only where the responsible person complies with the conditions referred to in Column 3 of the table.

However, this Notice of Exemption does not exempt the responsible person from the provisions specified in Column 2 where the relevant waste is received at premises that are, despite this exemption, required to be licensed for waste disposal (application to land) activities under the provisions of the Act.

- 5.2. Where a responsible person complies with the conditions of this Notice of Exemption, the activity referred to in Schedule 1 from which that person is exempt is taken to be a non-scheduled activity for the purposes of the Act.

Table 1

Column 1	Column 2	Column 3
Responsible person	Provisions from which the responsible person is exempt	Conditions to be met by the responsible person
Generator	section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation	all requirements specified in section 7 and 8
Processor	section 48 of the Act in respect of clause 39 of Schedule 1 to the Act Part 3 of the Regulation	all requirements specified in section 7 and 9
Consumer	section 48 of the Act in respect of clauses 39 and 42 of Schedule 1 to the Act Part 3 of the Regulation section 88 of the Act clause 47 of the Regulation	all requirements specified in section 7 and 10

This Notice of Exemption is a general exemption for the purposes of clause 51(3) of the Regulation.

Definitions

6. In this Notice of Exemption:

Blast furnace slag is a waste formed when iron ore, a mixture of oxides of iron, silica and alumina, a fuel consisting of coke, natural gas, oxygen and pulverised coal and limestone are fed into a blast furnace during the manufacture of iron for steel production.

Characterisation means sampling and testing that must be conducted on the blast furnace slag for the range of chemicals and other attributes listed in Column 1 of Table 2.

Composite sample means a sample that combines 5 discrete sub-samples into a single sample for the purpose of analysis.

Consumer means a person who applies, causes, or permits the application to land of blast furnace slag within the definitions of "application to land" in accordance with the Act. The consumer may be the landholder responsible for the land to which blast furnace slag is applied. Where a person responsible for transporting the blast furnace slag to the land application site is also the party applying the blast furnace slag, this person must meet the responsibilities of the consumer.

Generator means a person who generates, supplies, causes, or permits the supply of blast furnace slag to a processor or consumer. The generator may also be the processor.

NA means not applicable.

Once-off sampling means sampling and testing that must be conducted only once on a batch, truckload or stockpile of blast furnace slag that is not repeated, reproduced and does not form part of a continuous process.

Processor means a person who processes, mixes, blends, or otherwise incorporates blast furnace slag into a material for supply to a consumer.

Relevant waste means blast furnace slag that meets the requirements of Section 7.

Routine sampling means sampling and testing that must be conducted on the blast furnace slag on an ongoing and regular basis.

General conditions

7. This Notice of Exemption is subject to the following conditions:
 - 7.1. The chemical concentration or other attribute of the blast furnace slag listed in Column 1 of Table 2 must not exceed any of the following:
 - 7.1.1. the absolute maximum concentration or other value listed in Column 4 of Table 2,
 - 7.1.2. for characterisation or once-off tests, the maximum average (based on the arithmetic mean) concentration or other value listed in Column 2 of Table 2, and
 - 7.1.3. for routine tests, the maximum average (based on the arithmetic mean) concentration or other value listed in Column 3 of Table 2.
 - 7.2. The blast furnace slag can only be applied to land as an engineering fill in earthworks or for road making activities as follows:
 - 7.2.1. engineered fill,
 - 7.2.2. engineered pavements (base and sub-base coarse),
 - 7.2.3. filter aggregate
 - 7.2.4. asphalt aggregate
 - 7.3. The blast furnace slag can only be applied to land consistent with section 7.2 where:
 - 7.3.1. it complies with a relevant specification or Australian Standard or supply agreement/s, and
 - 7.3.2. planning or development consent that has specifically considered the use of blast furnace slag has been granted for the project.
 - 7.4. The blast furnace slag can be applied to land consistent with section 7.2 when blended with other exempted materials, provided that the blended materials have been validated as compliant with the conditions of each individual exemption, for the use specified in each exemption.

Generator responsibilities

8. The following conditions must be met by the generator for this exemption to apply:
 - 8.1. Sampling must be undertaken in accordance with Australian Standard 1141 Methods for sampling and testing aggregates (or equivalent). Sampling and information on sample storage and preparation must be detailed in a written sampling plan.
 - 8.2. Where the blast furnace slag is generated as part of a continuous process, the generator must undertake characterisation and routine sampling according to the requirements listed in Column 1 and Column 2 of Table 3, for the range of chemicals and other attributes listed in Column 1 of Table 2.
 - 8.3. Where the blast furnace slag is not generated as part of a continuous process, the generator may undertake once-off sampling of a batch, truckload or stockpile of blast furnace slag according to the requirements listed in Column 3 of Table 3, for the range of chemicals and other attributes listed in Column 1 of Table 2.
 - 8.4. Where there is a change in inputs that is likely to affect the properties in the blast furnace slag, characterisation must be repeated. Characterisation samples can be used for routine testing and subsequent calculations.
 - 8.5. Generators must keep a written record of all characterisation, routine and/or once-off test results for a period of five years.

- 8.6. Records of the quantity and proposed use of blast furnace slag supplied to the processor or consumer and the processor or consumer's name and address must be kept for a period of five years.
- 8.7. The generator of blast furnace slag must provide a written statement of compliance to the processor or consumer with each transaction, certifying that the blast furnace slag complies with the relevant conditions of this exemption.
- 8.8. The generator of blast furnace slag must make information on the latest characterisation and routine test results available to the processor and consumer.
- 8.9. The generator of blast furnace slag must use due diligence to ensure that the relevant waste is utilised in applications that are consistent with the conditions of this exemption.

Processor responsibilities

9. The following conditions must be met by the processor for this exemption to apply:

- 9.1. Records of the quantity and proposed use of blast furnace slag supplied to the consumer and the consumer's name and address must be kept for a period of five years.
- 9.2. Records of the quantity of blast furnace slag received by the processor from the generator, and the generators name and address, must be kept for a period of five years.
- 9.3. The processor of blast furnace slag must provide a written statement of compliance to the consumer with each transaction, certifying that the blast furnace slag complies with the relevant conditions of this exemption.
- 9.4. The processor of blast furnace slag must make information on the latest characterisation and routine test results available to the consumer.
- 9.5. The processor of blast furnace slag must use due diligence to ensure that the relevant waste is utilised in applications that are consistent with the conditions of this exemption.

Consumer responsibilities

10. The following conditions must be met by the consumer for this exemption to apply:

- 10.1. Records of the quantity and use of the blast furnace slag received by the consumer and the suppliers' name and address must be kept for a period of five years.
- 10.2. The blast furnace slag must not be applied in or beneath water including groundwater.
- 10.3. The consumer should note that regardless of having an exemption, the use of blast furnace slag remains subject to all other relevant environmental regulations within the Act and Regulations, including but not limited to land pollution (s142A) and water pollution (s120).
- 10.4. The consumer must land apply the relevant waste within a reasonable period of time.

Chemical and other material property requirements

11. This Notice of Exemption only applies to blast furnace slag where the chemical and other attributes listed in Column 1 of Table 2 comply with the chemical concentrations and other values listed in Column 2, Column 3 and Column 4 of Table 2, when analysed according to test methods specified in Column 5 of Table 2. Note that while limits are not included for boron and electrical conductivity, these must be tested in each sample and records kept of results.

Table 2

Column 1	Column 2	Column 3	Column 4	Column 5
Chemicals and other attributes	Maximum average concentration for characterisation (mg/kg 'dry weight' unless otherwise specified)	Maximum average concentration for routine testing (mg/kg 'dry weight' unless otherwise specified)	Absolute maximum concentration (mg/kg 'dry weight' unless otherwise specified)	Test method specified within Section
1. Mercury	0.5	Not Required	1	13.1
2. Cadmium	0.5	0.5	1	13.2
3. Lead	10	10	20	13.2
4. Arsenic	5	Not Required	10	13.2
5. Beryllium	10	Not Required	20	13.2
6. Boron	NA	NA	NA	13.2
7. Chromium (total)	50	Not Required	100	13.2
8. Copper	10	Not Required	20	13.2
9. Molybdenum	5	5	10	13.2
10. Nickel	10	Not Required	20	13.2
11. Selenium	2	Not Required	5	13.2
12. Zinc	25	25	50	13.2
13. Electrical Conductivity	NA	NA	NA	13.3
14. pH *	7.5 to 12.5	Not Required	7 to 13	13.3

*Note: The ranges given for pH are for the minimum and maximum acceptable pH values in the blast furnace slag.

Sampling and testing requirements

12. This Notice of Exemption only applies to blast furnace slag sampled according to the requirements in Table 3.

Table 3

Column 1	Column 2	Column 3
Characterisation sampling frequency	Routine sampling frequency	Once-off sampling frequency
20 composite samples, by taking 1 composite sample from a different batch, truckload or stockpile. This must be repeated every 2 years.	Either 5 composite samples per 10,000 tonnes or 5 composite samples per 6 months.	10 composite samples per 4,000 tonnes e.g. discrete once-off delivery or ship load.

Test methods

13. All testing must be undertaken by analytical laboratories accredited by the National Association of Testing Authorities, or equivalent. All chemicals and other attributes listed in Column 1 of Table 2 must be measured in accordance with the test methods specified below:

- 13.1. Test method for measuring the mercury concentration in blast furnace slag:
 - 13.1.1. Particle size reduction & sample splitting may be required.
 - 13.1.1.1. Analysis using USEPA SW-846 Method 7471B Mercury in solid or semisolid waste (manual cold-vapor technique), or an equivalent analytical method with a detection limit < 20% of the stated absolute maximum concentration in Table 2, Column 4 (i.e. 0.2 mg/kg dry weight).
 - 13.1.2. Report as mg/kg dry weight.
- 13.2. Test method for measuring chemicals 2 - 12 in blast furnace slag:
 - 13.2.1. Particle size reduction & sample splitting may be required.
 - 13.2.2. Sample preparation by digestion using USEPA SW-846 Method 3051A Microwave assisted acid digestion of sediments, sludges, soils, and oils.
 - 13.2.3. Analysis using USEPA SW-846 Method 6010C Inductively coupled plasma - atomic emission spectrometry, or an equivalent analytical method with a detection limit < 10% of the stated absolute maximum concentration in Table 2, Column 4 (i.e. 2 mg/kg dry weight for lead).
 - 13.2.4. Report as mg/kg dry weight.
- 13.3. Test methods for measuring the electrical conductivity and pH in blast furnace slag:
 - 13.3.1. Sample preparation by mixing 1 part blast furnace slag with 5 parts distilled water.
 - 13.3.2. Analysis using Method 103 (pH) and 104 (Electrical Conductivity). *In* Schedule B (3): Guideline on Laboratory Analysis of Potentially Contaminated Soils, National Environment Protection (Assessment of Site Contamination) Measure 1999 (or an equivalent analytical method).
 - 13.3.3. Report electrical conductivity in deciSiemens per metre (dS/m).

Exemption Granted

Christopher McElwain
Acting Waste Management
Environment Protection Authority
by delegation

Notes

The EPA may amend or revoke this exemption at any time. It is the responsibility of the generator, processor and consumer to ensure that they comply with all relevant requirements of the most current exemption. The current version of an exemption will be available on the EPA website: www.environment.nsw.gov.au

In gazetting this general exemption, the EPA is exempting the relevant waste from the specific requirements of the Act and Regulations as stated in this exemption. The EPA is not in any way endorsing the use of this substance or guaranteeing that the substance will confer benefit.

The EPA may grant specific exemptions in certain circumstances in recognition of intellectual property rights or where it is necessary to impose specific conditions on the use or application of a waste.

The use of exempted material remains subject to other relevant environmental regulations within the Act and Regulations. For example, a person who pollutes land (s142A) or water (s120), or does not meet the special requirements for asbestos waste (clause 42), regardless of having an exemption, is guilty of an offence and subject to prosecution.

For the purposes of arrangements between a generator, a processor and a consumer, a 'transaction' is taken to mean the contractual agreement between the two parties which specifies the exchange of waste material from one party to another. A 'statement of compliance' must be in writing and be provided with each transaction.

The conditions set out in this exemption are designed to minimise the risk of potential harm to the environment, human health or agriculture, however, neither this exemption nor these conditions guarantee that the environment, human health or agriculture will not be harmed.

The consumer should assess whether or not the exempted material is fit for the purpose the material is proposed to be used and whether this use will cause harm. The consumer may need to seek expert engineering or technical advice.

This exemption does not apply to any material received at a premises that is required to be licensed for waste disposal (application to land) activities under the provisions of the Act. This exemption does not remove the need for a site at which processing occurs to be licensed, if required under Schedule 1 of the Act.

This exemption does not alter the requirements of any other relevant legislation that must be met in utilising this material, including for example, the need to prepare a Material Safety Data Sheet (MSDS).

Regardless of any exemption provided by the EPA, the person who causes or permits the application of the substance to land must ensure that the action is lawful and consistent with the development consent requirements of the land.

All records required to be kept under this exemption must be made available to authorised officers of the EPA upon request.

Failure to comply with the conditions of this Notice of Exemption may constitute an offence under clause 51 of the Regulation and the responsible person will be required to comply with the normal regulatory provisions.

CONTACT US

t 1300 363 400
+61 3 9545 2176
e enquiries@csiro.au
w www.csiro.au

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FOR FURTHER INFORMATION

Energy Technology
David Harris
t +61 7 3327 4617
e David.Harris@csiro.au
w www.csiro.au/energy