USE OF COAL ASH IN MINE BACKFILL AND RELATED APPLICATIONS

RESEARCH REPORT 62

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August 2006
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Context Statement

Coal utilisation generates large amounts of end products which are mostly disposed of in repositories such as dams, dry ash disposal systems and landfill. In achieving sustainability of coal combustion there is a need to address the issue of waste generation comprehensively, and to provide the information enabling more ecological sensitive and cost effective methods for waste management and utilisation to be put in place.

Mine backfill with coal combustion products (CCPs) is gaining increasing attention by the power and mining industries as an emergent beneficial solution for ash disposal. Mine filling with CCPs is a recent and rapidly growing use for ash in USA and other countries. However, only a limited amount of investigation has been done to assess the suitability of ashes from Australian coals for beneficial use in the mining environment. Assessment methods and protocols for managing environmental risks are not currently available.

In mid 2005, CCSD in collaboration with the industry partners including Western Power, Griffin Coal, Tarong Energy and CS Energy, initiated study on the Environmental Assessment of Fly Ash for Use in Mine Backfill Applications. The research aims to provide a scientifically sound basis for removing some of the potential regulatory and perceived environmental risk issues that might otherwise act as impediments to economic use of coal ash in mine backfill applications, and at the same time to develop a generic protocol for matching individual ashes with specific mine-site requirements.

An initial requirement of the project was for a literature survey on the identification and assessment of environmental risks associated with the backfilling of mines and similar sites with ash or mixtures of ash and other materials (e.g. overburden or preparation refuse), to identify the available options for ash use in mine backfill, technical factors that might need to be considered, and the key issues affecting adoption of such beneficial use programs by the Australian coal industry.

This report represents the first in a series of deliverables for this project. A comprehensive summary of the purposes for which ash has been used in and around mine sites is given, along with the methods by which ash suitability has been evaluated.

Based on the findings of this survey, some programs are proposed by which the environmental impact of ashes for use in Australian mines might be evaluated. The feasibility of these will be further investigated as part of the CCSD project.

Future reports will include a more in-depth summary of relevant regulatory requirements for mine-site ash emplacement, and reports on trials of relevant test programs.

Lila Gurba
CCSD Research Manager
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EXECUTIVE SUMMARY

Coal ash and other combustion products may be used as backfill in open-cut or underground coal mines for a number of beneficial purposes. These include:

- Void infilling, spoil pile re-contouring or highwall reclamation;
- Grouting or infilling to control subsidence, ground movement or water flow;
- Amelioration of unfavourable water quality (e.g. acid pH) associated with mining;
- Provision of construction materials for mine access and haulage roads;
- Stabilisation of exposed rock, tailings or soil to prevent wind or water erosion;
- Control of contaminant migration, underground fires or spontaneous combustion;
- Improvement of natural or artificial soils in mine-site rehabilitation programs.

Although ash has been successfully used in a number of Australian coal mines for many of the purposes listed above, use of ash as mine backfill in Australia is still relatively limited, and indeed appears to have declined slightly in recent years. Significant quantities of ash are used for mine backfill, however, in the USA and Europe, reducing inter alia the land use and environmental impacts associated with other ash disposal options, and also providing benefits to assist the mining operation.

Regulatory barriers in Australia, under which ash could be considered as an industrial waste, tend to inhibit further beneficial ash usage. The environmental effects of the use of ash for mine backfill are also somewhat uncertain. Although most reviews have indicated ash use as backfill to be environmentally beneficial, or at least have no negative effect, some authors have suggested that negative effects do occur, and may result in contamination of water resources.

The main beneficial use of ash for mine backfill has traditionally been derived from the interaction of alkaline ash with mine solids, mine waters or in mining voids to ameliorate acid mine drainage conditions. Significant research has been carried out on the behaviour of different ashes in such applications, with a focus on the extent to which the ash may release or adsorb any potentially toxic elements in conjunction with the neutralisation process. Ash is also, however, routinely emplaced in open-cut mines as part of void infill programs in the western USA, without necessarily an AMD treatment objective in mind, and this may provide a better parallel for Australian conditions.

Although backfilling is common in underground metalliferous mines, only limited use has been made of backfill in underground coal mines, especially in Australia. Apart from its role in acid neutralisation, the ash-based backfill in underground mines is mainly used for ground support and subsidence control, for which the critical factors are geotechnical properties, such as flowability, density, porosity, abrasiveness, strength and pozzolanic or cementitious properties. Most Australian studies on the use of ash in underground coal mines have therefore focussed on the relation of ash characteristics to the geotechnical properties of the fill, rather than on any environmental issues which may arise. Fly ash has also been used for the control of mine fires, as a contaminant barrier to reduce the escape of waterborne contaminants from potentially toxic mine products such as preparation tailings, and as an additive to enhance the fertility of mine soils in reclamation programs.

Environmental evaluation of ash use in mine backfill, whether in open-cut or underground operations, requires consideration of a three-component system, involving interactions between the ash, mine water or groundwater, and the enclosing rock strata. Recent
research within CCSD has been directed towards an understanding of the two-component ash-water system, but a work program is proposed in this report to extend this research to encompass the wider interactions in the ash-water-rock system as well.

It is proposed that two different test routines be investigated as a basis for evaluating ash behaviour in mine backfill systems, using ash, water and relevant rock samples from selected mine sites. One of these is a two-step routine, in which the ash and mine water are brought together to produce a leachate, after which that leachate is brought into contact with samples of the mine rock materials. The leachates from both stages of the process will be analysed, and the results evaluated in the light of the solid phase and water characteristics and, to the extent possible, hydrogeochemical modeling techniques. The other routine involves the use of leachability tests directly on appropriate mixtures of the ash and rock materials. This may provide a more rapid basis for testing, but will need to be evaluated in the first instance against results from the two-stage process.

It is also envisaged that, in due course, the results of laboratory tests will be evaluated in the light of on-site monitoring groundwater programs, before and after ash emplacement.
1. INTRODUCTION

The extraction of coal and other mineral resources, whether by open-cut or underground techniques, inherently results in the creation of mining-induced voids that need to be managed in some way. Placement of backfill is one of the tools that may be used to assist in managing these voids, with associated benefits to the stability, safety, resource recovery and environmental impact of the mining operation. If the fill is a material that would otherwise be discarded elsewhere as an unwanted by-product, backfilling may also provide a mechanism for reducing the cost and impact of establishing a separate waste disposal process.

Ash from coal-fired power stations is one of a number of materials that may be used in mine backfill, whether for coal or metalliferous mining operations (Potvin et al., 2005). Other materials that may be used include waste rock such as overburden, natural sands or gravels, and coarse or fine reject materials from preparation plants. Cement and/or pozzolans (including ash) may be added to bind the particles together and strengthen the mass. Fly ash, slag, gypsum and lime may be added for this purpose, as well as a range of rheology and hydration modifiers, de-foaming agents, and durability enhancing components.

Ash has a number of advantages for use in coal mining, such as favourable geomechanical properties (including cementitious or pozzalanic characteristics), a capacity for placement in flowable paste or slurry form, and availability in large quantities from power stations near many mine sites. It may also have chemical properties that can be used to ameliorate other mine-related problems, such as the generation and discharge of acid waters from particular mining operations.

The use of ash in backfill for coal mining may be directed towards one or more of the following objectives:

a) Void infilling, spoil pile re-contouring or highwall reclamation in active or previously-abandoned open-cut mines;
b) Grouting or infilling of active or abandoned underground openings to control subsidence, ground movement or water flow;
c) Amelioration of unfavourable water quality (e.g. acid pH) associated with surface or underground exposures, mine overburden or preparation refuse emplacements;
d) Provision of base, sub-base or embankment fill for construction of mine access and haulage roads;
e) Stabilisation or cementing of soil cover or overburden emplacements to prevent wind or water erosion;
f) Provision of a sealing medium to control water seepage or contaminant migration, or to deal with underground fires and spontaneous combustion problems;
g) Improvement of water retention and fertility of natural or artificial soils, to enhance plant cover or assist crop growth as part of mine-site rehabilitation programs.

Ash may also be incorporated into concrete for construction of mine facilities, in a similar way to its use in civil engineering and building projects.
Coal ash may be therefore used by the mining industry for a variety of beneficial purposes. These include:

- improvement of geotechnical conditions,
- improvement of mine water quality,
- improvement in post-mine landscaping, and
- improvement in the growth of post-mining vegetation.

The present review is focused mainly on those aspects of ash utilisation at mine sites involving relatively deep burial, such as infilling of voids or improvement of ground conditions, and the associated interactions of the ash with other mine rocks and the local or regional groundwater system (Figure 1). Applications that involve interaction with living plant communities, such as in soil amendment and similar applications, are also discussed briefly, but these are the prime focus of separate research by the Ash Development Association of Australia (ADAA), and a related CCSD-ADAA research proposal to the Australian Coal Association Research Program (ACARP).

![Diagram showing relationship of CCSD research in mine backfill applications to wider-ranging CCSD and ADAA ash research activities.](Image)

Ash used in the non-soil aspects of mining operations (a to f in the list above) may be expected to interact with the surrounding ground and surface water, and also with the other rock materials in or around the emplaced ash body. Environmental evaluation of these interactions is mainly directed towards assessing the potential impacts of the ash on ground and/or surface water systems, with a focus on the liberation of chemical contaminants and possibly suspended solid components. Such evaluations have similar objectives to those associated with ash ponds and other emplacements at power stations, except that a three-component system involving ash, rock and water needs to be
considered, rather than one involving ash and water alone. The nature of the water may also be different to that encountered at conventional ash emplacement sites.

Use of ash as a soil amendment for mine-site revegetation programs, and also for use in more general agricultural and horticultural production, involves a four-way system of interactions: ash, rock/soil, water, and living plant organisms. The chemical conditions associated with the interactions in the soil zone are generally quite different from those to which the ash would be exposed as backfill in the deeper subsurface, with differences in \( \text{Eh}, \text{pH}, \) organic complexation and biological activity leading to significant differences in element mobility, compared to those in the soil environment. The migration paths, tolerances, benefits and impacts of the ash constituents in the soil and backfill environments are also quite different. Evaluation of ash for soil applications inherently involves biological as well as chemical considerations, while ash evaluation associated with subsurface backfill involves chemical considerations, either alone or in association with geotechnical factors. The placement technology and monitoring are also different, with an emphasis on water quality from wells in backfill applications and on plant yield and tissue composition in soil amendment studies.

2. CHARACTERISTICS AND UTILISATION OF AUSTRALIAN FLY ASHES

The fly ashes produced in Australian power stations are light to mid grey in colour, with irregular to spherical particles ranging from <1 \( \mu m \) to >200 \( \mu m \) in size (Heidrich, 2003). The majority of the ash is categorised as Type F under the ASTM classification system (ASTM, 1999), with silica and alumina representing 80-85% of the total chemical constituents.

![Figure 2: Size frequency distribution of selected Australian fly ashes. The heavy line at 45\( \mu m \) is the test sieve size used in AS3582.1 for fly ash classification.](image-url)
As shown in Figure 2, Australian fly ashes typically exhibit a bi-modal particle size distribution. Two populations can be clearly distinguished on the basis of the major mode: one with a major mode of 10-20µm and the other with a major mode of 35-80µm. All samples have a second minor mode at approximately 0.3µm. There is no apparent correlation of particle size distribution with either coal type or the particle collection technology employed, suggesting that other factors such as the particle size of the coal feed and the boiler operating conditions may be important in determining the ash particle size distribution. The particle size distribution of Australian ashes is similar to that reported for overseas fly ashes (Bayat, 1998; Moreno et al., 2005; Fernández-Jiménez and Palomo, 2003) although the size distribution may vary. As shown in Table 1, the percentage of ash passing a 45 µm sieve is one of the criteria used in the classification of fly ashes according to AS3582.1, which details the use of fly ash in Portland and blended cements. Most Australian ashes would be classified as fine ashes, with a few falling into the medium and coarse classifications.

Table 1: Classification of fly ash according to Australian Standard 3582.1

<table>
<thead>
<tr>
<th>Grade</th>
<th>Fineness (minimum mass % passing a 45µm sieve)</th>
<th>Loss on Ignition (% maximum)</th>
<th>Moisture content (% maximum)</th>
<th>SO₃ Content (% maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>75</td>
<td>4.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Medium</td>
<td>65</td>
<td>5.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Coarse</td>
<td>55</td>
<td>6.0</td>
<td>1.0</td>
<td>3.0</td>
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</table>

Surface area measurements on a selection of Australian fly ashes (Table 2) show distinct groupings on a regional basis. Ashes from Western Australian power stations tend to have the highest BET and Langmuir surface areas and those from New South Wales the lowest, while ashes from Queensland power stations tend to have intermediate characteristics. The surface area values are within the ranges reported for Polish fly ashes by Sarbak et al. (2004) and for a series of European fly ashes by Moreno et al. (2005), but tend to be higher than those reported for a suite of Spanish fly ashes, for which the BET surface area values ranged from 0.51 to 1.34 m²/g (Fernández-Jiménez and Palomo, 2003).

Table 2: Surface area, pore diameter and density for selected Australian fly ashes

<table>
<thead>
<tr>
<th>Location</th>
<th>Western Australia</th>
<th>New South Wales</th>
<th>Queensland</th>
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<tr>
<td>Station No.</td>
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<td>9</td>
<td>10</td>
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<tr>
<td>BET Surface Area (m²/g)</td>
<td>9.65</td>
<td>11.16</td>
<td>8.64</td>
</tr>
<tr>
<td>Langmuir Surface Area</td>
<td>13.73</td>
<td>15.78</td>
<td>12.32</td>
</tr>
<tr>
<td>Micropore Area</td>
<td>5.48</td>
<td>7.80</td>
<td>4.74</td>
</tr>
<tr>
<td>BET Surface area (non-micropore)</td>
<td>4.17</td>
<td>3.36</td>
<td>3.90</td>
</tr>
<tr>
<td>Average Pore Diameter BET (nm)</td>
<td>4.35</td>
<td>2.77</td>
<td>4.79</td>
</tr>
<tr>
<td>He Pycnometer Density</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Water Density</td>
<td>2.07</td>
<td>2.23</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Note: nd = not determined
The He pycnometer density shows a limited range of 1.91 to 2.36 g/cm$^3$, similar to that exhibited by the water pycnometer density, which varies from 1.80 to 2.23 g/cm$^3$. Although the density differences can be correlated with the abundance of iron bearing minerals in the ash, there are exceptions, suggesting that glass compositions may also play a role in determining particle density. Nairn et al. (2001) found that, for four Queensland fly ashes, the densities of the iron-poor fly ashes were 2.03 and 2.12 g/cm$^3$ whereas those of the iron-rich fly ashes were 2.40 and 2.43 g/cm$^3$. Densities reported for European fly ashes tend to be higher (Moreno et al., 2005; Fernández-Jiménez and Palomo, 2003). A correlation of ash density with Fe content and Fe mineralogy was also noted, although there were exceptions, particularly at low densities, that could not be readily explained (Moreno et al., 2005).

Major element analyses for selected fly ashes are presented in Table 3. All ashes easily meet the sulphur content requirement of AS3582.1, being an order of magnitude lower than the maximum stipulated of 3 wt%. As noted above, all of the analysed ashes would be classified as type F of the ASTM classification (ASTM, 1999), and would meet the requirements of the various utilisation standards as outlined by French (2005). As indicated above, Nairn et al. (2001) noted that fly ashes from four Queensland power stations fell into two groups based on iron content. Within the low-iron group of ashes; one ash had significantly lower alkaline earth and sodium contents than the other. Alkaline earth and alkali contents were similar in the two high-iron ashes, with calcium being higher than in either of the low-iron ashes and magnesium values comparable to those found in one of the low-iron ashes. Although the feed coal was not identified, these differences are probably due mainly to coal type.

**Table 3: Major element analyses for selected Australian fly ashes**

<table>
<thead>
<tr>
<th>Location</th>
<th>New South Wales</th>
<th>Queensland</th>
<th>Western Australia</th>
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<tbody>
<tr>
<td>Station No.</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>65.9</td>
<td>65.78</td>
<td>61.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>27.6</td>
<td>26.93</td>
<td>22.4</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.1</td>
<td>1.64</td>
<td>7.6</td>
</tr>
<tr>
<td>CaO</td>
<td>0.4</td>
<td>0.35</td>
<td>3.3</td>
</tr>
<tr>
<td>BaO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.3</td>
<td>0.30</td>
<td>1.1</td>
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<tr>
<td>Na$_2$O</td>
<td>0.2</td>
<td>0.41</td>
<td>0.9</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.9</td>
<td>3.0</td>
<td>1.9</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.3</td>
<td>1.15</td>
<td>0.9</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.2</td>
<td>0.11</td>
<td>0.2</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.1</td>
<td>0.30</td>
<td>0.1</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

NB: Normalised for LOI., Bld = below detection limit.

When compared to the values for European fly ashes quoted by Moreno et al. (2005), the silica contents of the Australian ashes are distinctly higher, ranging from 44.5 to 76.7 wt% in comparison to the more restricted range of 28.5 to 59.6% for the European ashes. Alumina contents are comparable but, with the exception of the Western Australian ashes and some Queensland samples, iron contents are lower in the Australian ashes. Calcium and alkali contents also tend to be lower in the Australian fly ashes in comparison to the values given by Moreno et al. (2005).
Unlike the major element compositions, the trace element contents of Australian fly ashes show significant variation (Table 4). The ashes from Western Australia are enriched in Ba, Be, Co, Cr, Ni and Zn and depleted in Sb, whereas those from three New South Wales power stations (NSW #3, NSW #12 and NSW #13) tend to have elevated B and Hg values in comparison to the ashes from NSW #1 and NSW #2. This difference may reflect variations in coal type, as the feed coal for the former stations is sourced from the Hunter Valley and that of the latter two from the Western Coalfield.

A notable feature is the generally low levels of trace elements found in Australian fly ashes when compared to the values for European ashes reported by Moreno et al. (2005). Thus the As, B, Cd, Cu, Li, Sb, and V contents are lower; Ba, Cr, Ni and V contents also tend to be lower, apart from the Western Australian fly ashes, which have levels comparable to those found by Moreno et al. (2005). Cobalt, Hg, and Mo contents are generally lower or comparable, apart from the Western Australian ashes, in which these elements tend to be higher. Beryllium, Ge, Pb, Se, and Sn contents are comparable to the values quoted by Moreno et al. (2005). In comparison to Chinese fly ashes (Liu et al., 2004), Cu, V and Pb values are lower in Australian ashes; Zn and As values are comparable, apart from the higher values obtained for the Western Australian fly ashes. The low trace element content of the Australian ashes reported above is also evident when the materials are compared to ashes from the Eggborough power station in the United Kingdom (Spears and Martinez-Tarrazona, 2004). Nickel and Zn are the only elements present in higher concentrations in Australian ashes than at Eggborough, and then only in the Western Australian fly ashes.

Table 4: Trace element analyses for selected Australian fly ashes

<table>
<thead>
<tr>
<th>Location</th>
<th>New South Wales</th>
<th>Queensland</th>
<th>Western Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>As</td>
<td>12.4</td>
<td>4.0</td>
<td>6.58</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>25</td>
<td>56</td>
</tr>
<tr>
<td>Ba</td>
<td>393</td>
<td>420</td>
<td>653</td>
</tr>
<tr>
<td>Be</td>
<td>22</td>
<td>15</td>
<td>3.9</td>
</tr>
<tr>
<td>Cd</td>
<td>0.404</td>
<td>0.90</td>
<td>0.25</td>
</tr>
<tr>
<td>Co</td>
<td>11</td>
<td>10</td>
<td>5.6</td>
</tr>
<tr>
<td>Cr</td>
<td>49.6</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td>Cu</td>
<td>51.6</td>
<td>50</td>
<td>28.1</td>
</tr>
<tr>
<td>Ge</td>
<td>40</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>Hg</td>
<td>0.018</td>
<td>0.028</td>
<td>0.152</td>
</tr>
<tr>
<td>Li</td>
<td>180</td>
<td>28.0</td>
<td>47.9</td>
</tr>
<tr>
<td>Mn</td>
<td>87.5</td>
<td>200</td>
<td>899</td>
</tr>
<tr>
<td>Mo</td>
<td>8.1</td>
<td>5.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Ni</td>
<td>41.2</td>
<td>30</td>
<td>10.5</td>
</tr>
<tr>
<td>Pb</td>
<td>59</td>
<td>60</td>
<td>48</td>
</tr>
<tr>
<td>Sb</td>
<td>2.9</td>
<td>2.3</td>
<td>3.1</td>
</tr>
<tr>
<td>Se</td>
<td>5.15</td>
<td>4.69</td>
<td>4.28</td>
</tr>
<tr>
<td>Sn</td>
<td>10</td>
<td>12</td>
<td>5.7</td>
</tr>
<tr>
<td>V</td>
<td>128</td>
<td>120</td>
<td>48.5</td>
</tr>
<tr>
<td>W</td>
<td>4.5</td>
<td>6.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Zn</td>
<td>108</td>
<td>86</td>
<td>67.2</td>
</tr>
<tr>
<td>Zr</td>
<td>600</td>
<td>440</td>
<td>250</td>
</tr>
</tbody>
</table>
Quantitative X-ray diffraction analysis of selected Australian fly ashes (Table 5) shows amorphous alumino-silicate glass to be the dominant phase. Of the crystalline phases, quartz and mullite are dominant while the iron oxides hematite, maghemite and magnetite are minor components. Spinel, cristobalite and calcite are rare or trace phases present in some ashes. The ashes from Western Australia are distinctive in containing relatively abundant iron oxide phases, higher quartz and lower glass contents. Two of the Queensland ashes (5 and 14) also have relatively high iron oxide contents, similar to those of the Western Australian samples, while the remaining Queensland ash (7) is similar to New South Wales fly ashes. More variability is exhibited by the New South Wales fly ashes, with samples 3 and 13 containing more abundant iron oxide phases in contrast to samples 1, 2 and 12. This variation may reflect the mineralogy of the feed coal, an observation supported by the work of Ward and French (2005), which has shown that relationships exist between the mineralogy of the feed coals (as determined by quantitative X-ray diffractometry of the oxygen plasma ash residues) and the resultant fly ash.

Nairn et al. (2001) obtained similar results for a series of Queensland fly ashes, in which amorphous glass accounted for about 70% of the fly ash. Quartz and mullite were the dominant crystalline phases in both the iron-poor and iron-rich groups, with ferrite spinel also being present in the iron-rich ashes. Little comparative data are available, however, for overseas ashes. In a study of fly ash from a Japanese power station, Lee et al. (1999) found mullite and quartz to be the dominant crystalline phases, although the mullite contents were consistently higher (12.6-17.3 wt%) and the glass contents correspondingly lower (66.7–78.5 wt%). Moreno et al. (2005) found considerably greater variability in their study of European fly ashes. While amorphous alumino-silicate glass was still the dominant phase identified, glass contents varied from 48 to 86 wt%, quartz from 1.7 to 12.5 wt%, and mullite from <0.3 to 40.4 wt%. Calcite was found in only two of the ashes analysed by Moreno et al. (2005), but lime and anhydrite were found in several of the European ashes, in proportions varying from <0.3 to 5.8 wt % and <0.3 to 15.0 wt% respectively. While hematite was found to be relatively uncommon, magnetite was present in all of ashes studied, reaching a maximum of 3.8 wt%. Feldspar was an uncommon phase and ettringite was rare, being found in only one ash sample.

**Table 5: Quantitative X-ray diffraction mineralogy of selected Australian fly ashes**

<table>
<thead>
<tr>
<th>Location</th>
<th>New South Wales</th>
<th>Queensland</th>
<th>Western Australia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Station number</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Quartz</td>
<td>4.9</td>
<td>11.2</td>
<td>9.7</td>
</tr>
<tr>
<td>Mullite</td>
<td>8.5</td>
<td>16.0</td>
<td>10.2</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>0.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Spinel</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>0.0</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Maghemite</td>
<td>0.1</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.0</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>86.4</td>
<td>72.0</td>
<td>78.1</td>
</tr>
</tbody>
</table>
2.1. Utilisation of Australian Ash Products

Australian fly ash typically has geotechnical characteristics similar to those of medium to dense sand (Heidrich, 2003), but a compacted density of only around 60% that of dense sand. It therefore represents material with a high strength and relatively a low bulk density, the combination of which enhances its applicability for backfilling retaining walls or for use in construction embankments on soft soil materials. Other mechanical properties relevant to such applications include:

- High internal angle of friction;
- Low compressibility;
- Ease of compaction;
- Low settlement when used as fill material.

Australian ashes are generally pozzolanic, and can be used in conjunction with other cementitious materials (e.g. Portland and slag cements) to enhance the characteristics and performance of concrete. Use of ash in this way, in preference to extraction of other raw materials, has additional benefits in reducing Australia’s nett greenhouse gas emissions (Heidrich et al., 2005). Of the 13.01 Mt of ash produced in Australia in 2003, a total of 1.42 million tonnes were sold for use in cementitious applications and 0.5 Mt for non-cementitious applications (Heidrich et al., 2005). A further 2.45 Mt of ash was used in projects offering some sort of beneficial use, including mine site remediation and haul road construction.

Beneficial use includes usage internally by the ash producer as well as transfer or sales of ash to other bodies for beneficial application. Placement of ash in ponds is not considered to represent beneficial use.

As indicated in Table 6, the level of beneficial use has increased substantially since 1994, due to use of ash for bulk fill applications and for use in backfilling of mines in South Australia and New South Wales. Use of ash for this purpose, however, has declined somewhat since 1998, and in 2003 was around half of the level achieved at the peak of such applications. Fly ash was also extensively used in construction of Olympic venues such as the Penrith Whitewater stadium (Heeley and Shirtley, 2001).

Table 6: Australian ash production and sales (ADAA data)

<table>
<thead>
<tr>
<th>Year</th>
<th>Ash Production $\times 10^3$ t</th>
<th>Cementitious Ash Sales $\times 10^3$ t</th>
<th>Total Ash Sales $\times 10^3$ t</th>
<th>Other Beneficial Ash Usage $\times 10^3$ t</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>8,145</td>
<td>614</td>
<td>722</td>
<td>nr</td>
</tr>
<tr>
<td>1991</td>
<td>8,340</td>
<td>592</td>
<td>696</td>
<td>nr</td>
</tr>
<tr>
<td>1992</td>
<td>8,451</td>
<td>603</td>
<td>709</td>
<td>776</td>
</tr>
<tr>
<td>1993</td>
<td>8,510</td>
<td>661</td>
<td>780</td>
<td>850</td>
</tr>
<tr>
<td>1994</td>
<td>8,865</td>
<td>722</td>
<td>902</td>
<td>980</td>
</tr>
<tr>
<td>1995</td>
<td>9,290</td>
<td>735</td>
<td>1,275</td>
<td>1,910</td>
</tr>
<tr>
<td>1996</td>
<td>9,680</td>
<td>750</td>
<td>842</td>
<td>3,210</td>
</tr>
<tr>
<td>1997</td>
<td>9,980</td>
<td>1,020</td>
<td>1,140</td>
<td>4,545</td>
</tr>
<tr>
<td>1998</td>
<td>10,980</td>
<td>1,178</td>
<td>1,363</td>
<td>5,393</td>
</tr>
<tr>
<td>1999</td>
<td>11,416</td>
<td>1,165</td>
<td>1,323</td>
<td>3,809</td>
</tr>
<tr>
<td>2000</td>
<td>11,770</td>
<td>1,161</td>
<td>1,522</td>
<td>3,901</td>
</tr>
<tr>
<td>2001</td>
<td>12,182</td>
<td>1,229</td>
<td>1,618</td>
<td>2,158</td>
</tr>
<tr>
<td>2002</td>
<td>12,510</td>
<td>1,353</td>
<td>1,827</td>
<td>2,210</td>
</tr>
<tr>
<td>2003</td>
<td>13,010</td>
<td>1,420</td>
<td>1,925</td>
<td>2,450</td>
</tr>
</tbody>
</table>

Note: nr = not recorded
2.2. Ash Use in Other Countries

In 2000 almost 1 billion tonnes of coal was burned in the United States (Kalyoncu, 2001), which generated 120 million tonnes of ash and other coal combustion products (CCPs). Electric utilities alone burned over 860 million tonnes of coal and generated over 98 million tonnes of CCPs (Table 7).

Almost 25 million tonnes of the CCPs produced in the US in 2000 were used in various ways, mainly in cement and concrete, structural fills, waste stabilization, road base/sub-base, and mining applications. A total of 1.1 Mt of fly ash, 330,000 t of bottom ash and 166,000 t of FGD residues were used in mining applications. As indicated in Figure 3, these represent around 7% and 10%, respectively, of the total usage of fly ash and bottom ash materials.

The figures for mining use, however, are perhaps somewhat misleading. While Table 7 shows that only around 1.5 Mt of CCPs were used for mine applications in the USA in 2000, Young (2002) indicates that around 4 Mt of CCPs (fly ash, bottom ash and FGD sludge) per year have been used for some time as part of the backfill for two open-cut mines (operated by BHP-Billiton) in the San Juan Basin of New Mexico. Koehler (2002) indicates that a further 0.4 to 0.5 Mt of ash per year have been and are being used as backfill in another western US open-cut operation.

Data for a number of other countries are provided in Table 8. Information from the European Union has been combined under data provided by the European Coal Combustion Products Association (ECOBA), member countries of which are Belgium, France, Germany, Greece, Ireland, The Netherlands, Poland, Portugal, Spain, and the United Kingdom. These countries represent over 90% of the total CCP production in Europe (Kalyoncu, 2001).

Table 7: Production and use of ash and other CCPs in the USA (thousand tonnes), 2000 (Kalyoncu, 2001)

<table>
<thead>
<tr>
<th>Production/Use</th>
<th>Fly ash</th>
<th>Bottom ash</th>
<th>Boiler slag</th>
<th>FGD material</th>
<th>Total CCPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>13</td>
<td>4</td>
<td>--</td>
<td>--</td>
<td>69</td>
</tr>
<tr>
<td>Blasting grit-roofing granules</td>
<td>--</td>
<td>133</td>
<td>1,900</td>
<td>--</td>
<td>2,030</td>
</tr>
<tr>
<td>Cement clinker raw feed</td>
<td>1,030</td>
<td>158</td>
<td>--</td>
<td>--</td>
<td>2,290</td>
</tr>
<tr>
<td>Concrete, masonry</td>
<td>9,600</td>
<td>331</td>
<td>(3')</td>
<td>318</td>
<td>10,300</td>
</tr>
<tr>
<td>Floculent fill</td>
<td>632</td>
<td>10</td>
<td>16</td>
<td>30</td>
<td>688</td>
</tr>
<tr>
<td>Mineral filler</td>
<td>108</td>
<td>93</td>
<td>11</td>
<td>(3')</td>
<td>212</td>
</tr>
<tr>
<td>Mining applications</td>
<td>1,050</td>
<td>333</td>
<td>--</td>
<td>166</td>
<td>1,250</td>
</tr>
<tr>
<td>Roadbase/subbase</td>
<td>1,100</td>
<td>739</td>
<td>(3')</td>
<td>85</td>
<td>1,940</td>
</tr>
<tr>
<td>Snow and ice control</td>
<td>3</td>
<td>755</td>
<td>55</td>
<td>--</td>
<td>811</td>
</tr>
<tr>
<td>Soil modification</td>
<td>142</td>
<td>25</td>
<td>--</td>
<td>--</td>
<td>127</td>
</tr>
<tr>
<td>Structural fills</td>
<td>2,370</td>
<td>1,230</td>
<td>32</td>
<td>496</td>
<td>4,130</td>
</tr>
<tr>
<td>Wallboard</td>
<td>--</td>
<td>--</td>
<td>3,020</td>
<td>--</td>
<td>3,020</td>
</tr>
<tr>
<td>Waste stabilization-solidification</td>
<td>1,600</td>
<td>32</td>
<td>--</td>
<td>19</td>
<td>1,652</td>
</tr>
<tr>
<td>Other</td>
<td>413</td>
<td>571</td>
<td>89</td>
<td>173</td>
<td>1,230</td>
</tr>
<tr>
<td>Total</td>
<td>18,200</td>
<td>4,480</td>
<td>2,116</td>
<td>4,380</td>
<td>24,800</td>
</tr>
<tr>
<td>Individual use percentage</td>
<td>31.90</td>
<td>29.20</td>
<td>86.50</td>
<td>18.80</td>
<td>NA</td>
</tr>
<tr>
<td>Cumulative use percentage</td>
<td>21.90</td>
<td>31.30</td>
<td>33.10</td>
<td>29.70</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA Not available. -- Zero.
1/ Total CCPs include Categories I and II: Dry and Ponded respectively.
2/ FGD, fine gas desulfurization.
3/ Less than 1/2 unit.
Table 8: Production and use of CCPs in other selected countries (Mt), 2000 (Kalyoncu, 2001).

<table>
<thead>
<tr>
<th>Country or Region</th>
<th>Fly Ash</th>
<th>Bottom Ash</th>
<th>Other CCPs</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Prod’n</td>
<td>Use</td>
<td>Prod’n</td>
<td>Use</td>
</tr>
<tr>
<td>ECOBA</td>
<td>37.14</td>
<td>18.17*</td>
<td>5.62</td>
<td>2.50*</td>
</tr>
<tr>
<td>Canada</td>
<td>5.00</td>
<td>1.10</td>
<td>1.60</td>
<td>0.20</td>
</tr>
<tr>
<td>Japan</td>
<td>6.50</td>
<td>5.25</td>
<td>1.20</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Note: * excludes landfill

The ECOBA profitably used 56% (31 Mt) of the 54.5 Mt of CCPs generated by its member countries in 2000, compared with a usage rate of about 30% by the United States. Over 18 Mt of 37 Mt fly ash produced was used (48% usage rate), along with a slightly smaller fraction of bottom ash (44%). Raw material shortages and favourable state regulations account for the higher use rates of CCPs in Europe. As in Australia and the USA, the main usage was in concrete (37%), followed by Portland cement manufacture (31%) and road construction (21%). An additional 18.35 Mt of CCPs (not tabulated), mainly fly ash (15.43 Mt) and bottom ash (2.05 Mt) were used in landfill applications.

Canada used about 1.9 Mt (27%) of the 7 Mt CCPs produced (Table 8). In Japan 1999 figures were 9.1 Mt and 7.65 Mt for production and use, respectively. These figures represent a usage rate of 84%. High disposal costs for CCPs in Japan ($US100.00 per tonne) make many usage alternatives economically viable. India generated about 90 Mt of CCPs in 1999 (not tabulated), of which about 11.7 Mt (13%) was used, and Israel generated 1.2 Mt, of which 1.05 Mt (87%) was used.

Figure 3: Proportion of fly ash (left) and bottom ash (right) used for different purposes in the USA during 2000 (Kalyoncu, 2001).
Vom Berg and Feuerborn (2005) indicate that around 65 Mt of CCPs were produced by European (EU 15) power plants in 2003, of which some 68% was represented by fly ash (Figure 4). Most of these CCPs produced were used in the construction industry, in civil engineering and as construction materials in underground mining (52.4 %) or for restoration of open cast mines, quarries and pits (35.9 %). In 2003 about 8.0 % of European CCPs were temporarily stockpiled for future utilisation and 3.7 % were subject to disposal in some way. A total of 47 % of the fly ash, 44 % of the bottom ash, 100 % of the boiler slag and 51 % of the FBC ash were utilised in the construction industry and in underground mining. Less than 3 % of the fly ash, 10 % of the bottom ash and 29 % of the FBC ash had to be disposed of because they could not be used.

The utilisation rates of fly ash and bottom ash in the construction industry and in underground mining within the EU 15 region have increased continually in recent years. More specifically, the utilisation rate of fly ash increased from 34 % in 1993 to 47 % in 2003, and the usage rate for bottom ash rose from 25 % in 1993 to 44 % in 2003. The utilisation rates for fly ash and bottom ash both reached maxima of 48% and 44% respectively in 1999. The decrease in the utilisation rate for these materials from 1999 to 2000 can be attributed to higher production combined with a constant utilisation level (18.2 million tonnes for fly ash and 2.5 million tonnes for bottom ash). An increase in the utilisation rate by the construction industry and in underground mining was counterbalanced by a decrease in the utilisation rate for restoration of open cut mines, pits and quarries, and a decrease in emplacement at special disposal sites.

Ten new members, most of them from Eastern Europe, joined the EU in June 2004. Coal or lignite is used as a fuel for power production in eight of those ten countries, and, although exact figures are not available, the total amount of CCPs produced is estimated at about 30 million tonnes annually. Most of the fuel burned is sub-bituminous coal or lignite, and the pattern of utilisation and the utilisation rates are undoubtedly different to those of the ECOBA members or the EU 15 countries.

3. INTERACTION OF COAL ASH WITH WATER

The individual particles in Australian fly ashes are made up mainly (50-80%) of aluminosilicate glass, with additional but relatively minor proportions of crystalline phases including quartz, mullite, cristobalite, haematite and magnetite (Ward and French, 2003). Those produced in other countries are similar (Hower et al., 1999; Winburn et al., 2000), although the relative proportions may be assessed by different techniques. The
various trace elements may occur as part of the crystalline phases, within the aluminosilicate glass, or as coatings adsorbed on the surfaces of the individual ash particles (Jankowski et al., 2005).

Sear et al. (2003) suggest that, when water is added to coal ash, sulphate deposited on the particle surfaces passes into solution as sulphuric acid, which initially lowers the pH of the ash-water system. However, in most cases this is only a transient situation, and the pH rises rapidly as calcium passes into solution from deeper layers on the ash surface. Ash with a high proportion of Ca may develop a pH of 11 or 12; lower values (8-9) may be associated with lower Ca contents, or with ashes that have been stored for some time in a lagoon or pond and lost some of the mobile Ca as a result of long-term leaching processes.

Ashes that do not have significant concentrations of Ca (or Mg), however, in relation to the sulphate (or SO$_3$) content, may not develop such high pH values, and retain the original acid pH characteristics. This situation applies to a number of ashes from Australian power stations. Killingley et al. (2000) and Jankowski et al. (2004a-c; 2005a-d), for example, indicate that some Australian ashes may develop acid pH values of around 4-5 on interaction with water, whereas others develop alkaline pH values of 11 or 12. The composition of the ashes depends largely on the mineral matter in the relevant feed coal (Ward and French, 2005); the relation between ash composition and the pH developed on interaction with water is summarised in Figure 5.

The pH of the ash-water system is a critical factor in determining the extent to which different major and trace elements are leached from individual ashes under different environmental conditions (Jankowski et al, 2004a-c, 2005a-d). Although many ashes throughout the world exhibit alkaline pH characteristics, not all ashes necessarily exhibit alkaline behaviour. The behaviour and use of acid-forming ashes in mine sites and other applications, however, have not been investigated to the same extent as those for the more common alkaline materials.

![Initial pH (column test) - Glass Composition](image)

**Figure 5.** Relation between pH of ash-water system, as indicated by column leaching studies (Killingley et al., 2000), and the chemical composition of the glass phase in the ash as indicated by XRD and chemical analysis (Ward and French, 2003).
4. REGULATORY ISSUES

4.1. Australia

As indicated by Heidrich (2003), Australian ash producers are increasingly regarding the “effective utilisation” of ash materials as a high priority issue, and at the same time recognise the potential development of a significant challenge as a consequence of deregulating electricity markets. Open contestability of electricity supply markets has presented power station operators with many challenges beyond the simple task of reducing costs and increasing profitability. With proposed transfers from Government ownership to private sector control, a number of previously “taken for granted” political protections afforded to power stations as Government Trading Enterprises (GTEs) are likely to disappear.

However, as also indicated by Heidrich (2003), a number of barriers exist in Australia that inhibit wider use of coal combustion products for beneficial purposes. Interpretations of current legislation (Aynsley et al., 2003; Riley, 2005) suggest that, regardless of any recycling to which the material may be subjected, coal ash is still considered to be an industrial waste, and as such is subjected to greater environmental controls than equivalent virgin (e.g. directly mined) materials with equivalent potential impacts. This has the effect of making virgin materials more attractive than recycled materials, even though the recycled materials (ash) may be equally if not more suitable for the purpose.

As an example, each State operates under its own Environment Protection Act and operational regulations. Ash with identical properties may be classed as “inert waste” in one State but as “prescribed waste” in another. This has impacts on interstate trade in ash products, and makes dealing with ash different under each state jurisdiction. The utilisation of coal ash and other products, particularly but not only in agricultural applications, has recently come under further scrutiny, and this has highlighted both an absence of legislation and internal conflicts in existing legislation (Aynsley et al. 2003).

4.2. USA

In the USA the regulations that apply most particularly to the disposal of coal ash, especially for mine-site applications, are the Resource Conservation and Recovery Act (RCRA) and the Surface Mining Control and Reclamation Act (SMCRA). The United States EPA has concluded that fossil fuel combustion wastes do not warrant regulation as hazardous wastes, but that national non-hazardous waste regulations must be followed for coal combustion wastes disposed in surface impoundments and landfills and as mine fill (Riley, 2005). It is obligatory in the US to comply with the SMCRA requirements if ash is backfilled into surface mines (Vorries, 2001). Individual states may enact their own legislation, or defer to the federal legislation in this regard.

The requirements before and after any placement of ash into or on to US mine sites are extensive. In particular, they encompass:

- site characterisation, including geologic, hydrologic and land use information;
- a reclamation plan that “provides for protection of the environment, public safety, and, ideally, a new beneficial land use”; and
- acid or toxic drainage must be minimised;
• public participation; Citizens have the right to petition the Office of Surface Mining (OSM) “to initiate a proceeding for the issuance, amendment or repeal of any regulation under the SMCRA”; an application to place coal combustion waste is regarded as a major revision of a mining permit;
• ground water monitoring;
• environmental performance standards must be met, i.e.: “For disposal of non-coal mine waste, placement and storage shall ensure that leachate and surface runoff do not degrade surface or groundwater”. However, individual states differ in the interpretation of whether ash is a non-coal mine waste;
• compliance is required with relevant (state and federal) water quality and air quality regulations, as well as the Endangered Species Act;
• corrective action is required to minimise any adverse impacts due to non-compliance;
• placement engineering should minimise erosion and water pollution and support the approved post-mining land use; ash should not be disposed of in mined-out areas if spoil is displaced and requires another form of disposal; ash disposal must be in accordance with reclamation standards;
• a performance bond is required.

The US-EPA has identified a small number of unlined solid waste disposal facilities at electric power stations from which leachates appear to contain elements of toxicity determined to be detrimental to public health and/or the environment (Vorries, 2003), and feel that similarities between these sites and mine backfill installations may also warrant tighter regulation. However, as pointed out by Vorries (2001) in a discussion of the roles of the EPA and the Office of Surface Mining as regulatory bodies, any additional regulation of CCB placement at mine sites should only be based on sound scientific evidence that the existing regulatory framework is inadequate.

4.3. Europe and the United Kingdom

In the European Union, fly ash is not regarded as a “hazardous waste” unless it or its leachate contains a toxic substance or substances at such concentrations that the ash or leachate exhibits a “hazardous characteristic”. Although coal ash is defined as a non-hazardous waste in the European Waste Catalogue, ash from co-combustion is deemed to be a hazardous waste unless it is proved that it is non-hazardous. The disposal of ash in landfill is governed by the EU directives that apply to disposal in landfills generally. The relevant Council Directive (Riley, 2005) indicates that: “… like any other type of waste treatment, landfill should be adequately monitored and managed to prevent or reduce potential adverse effects on the environment and risks to human health”.

The UK Quality Ash Association (2005) and Sear (2003) provide a further summary of emerging UK and EU legislation affecting the emplacement of pulverised fuel ash (PFA), and also a summary of the diverse test methods for assessing the impact of the different ash materials.

5. ENVIRONMENTAL IMPACT OF ASH EMLACEMENT

Although PFA has been used in a wide range of applications in the United Kingdom since 1952 (Sear, 2003), increased interest in the impact of industry on the environment in
recent years has led to some questioning of the use of coal ash as a construction material. As part of the response to this situation, a comprehensive study was carried out by the University of Nottingham (Arnold et al., 2002) of the impact of PFA on the environment associated with large highway embankments of varying ages. This study indicated that the PFA in these embankments did not represent a significant source of groundwater contamination, and that agriculture and traffic inputs appear to be more significant than the PFA as contaminant sources.

Except for any materials added during combustion (e.g. co-fired biomass) or ash handling, the chemical elements contained within the ash are essentially the same elements that were in the original coal. Return of the ash to the mine site could thus be expected to re-establish a similar mixture of elements, in overall terms, to that existing in the subsurface strata before mining took place. The elements in the ash, however, have been concentrated by removal of the coal’s organic matter, and also reconstituted to occur in different ways after the combustion process. Their relative mobility and their potential impact on the groundwater regime may therefore be different to those associated with the same elements in the original in-situ coal bed.

A review of the impacts associated with placement of coal combustion products at coal mine sites by Vorries (2001) has indicated that: “all of the scientific evidence to date shows that placement of these materials at SMCRA mine sites has either been environmentally beneficial or had no negative effect”. Similar views are echoed by a number of other US studies (e.g. Murarka, 2001).

Norris (2004), however, has disputed this generalisation, providing several examples to show that negative impacts can arise from ash placement, and suggesting that they are common at sites where monitoring is performed at places and times that are capable of detecting impacts. Negative impacts on water resources in this context may include:

- contamination at a level high enough to impair or preclude a potential use for the water resource;
- increases in existing contamination or introduction of new contaminants;
- delay, deferral, extension or cessation of attenuation or remediation of an existing contaminated water resource;
- use of ash placement to justify an otherwise unacceptable project, with the project then resulting in contamination of a water resource;
- replacement of an existing pattern of contamination by a new contamination pattern.

6. USE OF ASH IN MINE BACKFILL APPLICATIONS

Ash is one of many materials that may be used for mine backfill (Potvin et al., 2005), whether for purposes such as stability improvement, subsidence control or mine-site rehabilitation. Other fills, especially in metalliferous mines, are based on components such as overburden rock and concentrator mill tailings, which are made up of essentially the same materials that were in the ground at the site before mining commenced. Unlike projects in which such mine-rock wastes are returned underground, however, the use of introduced and/or processed materials, such as ash, requires extensive geochemical characterisation of both the fill and the receiving environment, in order to prevent
contamination of groundwater or surface water supplies. As noted by Potvin et al. (2005), regulatory and public concerns about contaminant transport have prevented many worthwhile mine backfill projects from proceeding, with consequent loss of the beneficial use component in the overall waste management process.

6.1. Amelioration of Acid Mine Waters

The most widespread and best-known use of ash in non-soil mine backfill is probably the use of alkaline ash to ameliorate acid drainage conditions associated with surface and underground coal mines in areas such as South Africa and the eastern USA (e.g. Branam et al., 1999; Reeves et al., 2005; Surender and Petrik, 2005). As discussed more fully below, this may involve the use of ash for direct treatment of the mine water, placement of ash in the ground intimately mixed with acid-producing material, or use of ash to fill voids and restrict the interaction of air and/or water in the subsurface with acid-generating strata. Similar use may also be made of alkaline coal ash to ameliorate acid mine water in metalliferous operations.

Calcium and other elements in the ash serve to increase the pH of ground or surface water in such situations, and the ash may also provide a site for sorption or fixation of other mine water or mine soil contaminants (Mulligan et al., 2001). However, exposure to such an acid environment may also mobilise a number of elements from the ash (Daniels et al., 1999; Ziemkiewicz et al., 2003; Jankowski et al., 2004c), and a complex series of interactions involving ash, rock and water is inherently developed.

6.1.1. Formation of Acid Mine Drainage

Low pH waters resulting in acid mine drainage (AMD) or acid rock drainage (ARD) arise from the oxidation of pyrite in the exposed coal or rock materials. The interaction of pyrite, oxygen and water involves a series of reactions (Reynolds, 2005; Akcil and Koldas, 2005), which can be summarised as follows:

\[4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4\]

The exact process equations are very complex, and several minor variations may also occur. Bacteria are also thought to be involved in the process (O’Brien, 2000), especially Thiobacillus ferrooxidans, an acid-tolerant micro-organism that gains energy from the oxidation of inorganic compounds (Nordstrom and Southam, 1997) and catalyses the oxidation reactions.

Factors that determine the rate of acid generation in such situations (Akcil and Koldas, 2005) include:

- pH;
- temperature;
- oxygen content of the gas phase, if saturation <100%;
- oxygen concentration in the water phase;
- degree of saturation with water;
- chemical activity of Fe$^{3+}$;
- surface area of exposed metal sulphide;
- chemical activation energy required to initiate acid generation;
- bacterial activity.
In some cases the rocks in the surrounding strata may have a buffering effect and give rise to a leachate that is effectively pH-neutral (O’Brien, 2000), but in other cases the leachate may have a pH of 2 or lower and total dissolved solids (TDS) of 4,000-5,000 mg/l (Reynolds, 2005). The distribution and abundance of pyrite and calcite or dolomite in coals may be used to predict the extent of acidification and the potential for neutralisation of AMD in particular areas. A study of South African coals by Pinetown et al. (2005) indicated that, while the availability of carbonate minerals in the coal may provide a temporary buffering capacity, sufficient carbonates were not available in the coals studied for long-term neutralization of acid waters generated by the pyrite component.

Acid mine drainage may be derived from several different parts of the mine workings, with acid generation either taking place during mining or continuing after mining has ceased. Potential sources of AMD (Akcil and Koldas, 2005), either in metalliferous or coal mines, include:

- mine rock dumps;
- tailings impoundments;
- underground and open cut mine workings;
- pumped-out or naturally-discharging underground water;
- diffuse seeps from replaced overburden in rehabilitated areas;
- rock used in construction of roads, dams and other installations.

### 6.1.2. Use of Ash in Acid Mine Drainage Control

Ash may be brought into contact with acid mine drainage in a number of ways, in order to increase the pH of the mine water. The ash may be mixed with the acid water and the neutralized water and ash co-disposed in an appropriate manner (Surender and Petrik, 2005), or the ash may be intimately mixed with acid-generating solids, such as pyritic overburden or preparation refuse (Daniels et al., 1999), and the mixture emplaced in a similar way to other solid mine wastes. Acid-generating solids (e.g. pyritic overburden) may also be buried on-site (e.g. in overburden dumps) in such a way that they are surrounded by ash and/or other neutralising materials (Figure 6).

In other situations (e.g. underground mines) the ash may be used to introduce a low-permeability fill or grout to voids, fractures and other subsurface openings, reducing the exposure of acid-generating rocks to air or water and thus isolating pyritic materials from the oxygen needed for acid production (Reeves et al., 2005). Such usage can also help to control the pattern of subsurface water flow, limiting the escape of any acid waters from the mine site.

![Figure 6: Encapsulation of acid-generating mine waste by non-acid or neutralizing materials (including coal ash) in emplaced overburden at an open-cut operation (Thomas, 2002).](image-url)
6.2. Direct Treatment of Acid Mine Waters

The mixing of alkaline ash with acid waters to achieve pH neutralisation is one of a number of options that may be used for direct treatment of AMD at relevant mine sites. Other options include lime neutralisation and electrochemical protection. However, as indicated by Reynolds et al. (2005), such methods are costly, and require constant management. The waters produced by such treatments may also retain a range of heavy metals and other dissolved constituents, which, unless also removed, could prevent use for irrigation or other purposes.

6.2.1. Batch Leaching and Pilot Plant Studies

Surender and Petrik (2005) describe a series of studies at different scales to investigate the potential for using fly ash as a neutralising agent for acid mine waters in South Africa, with a view to full-scale site implementation. The work program for this study included the following components:

- identify suitable fly ash and AMD for treatment;
- conduct laboratory tests and optimize the co-disposal process;
- design, construct and commission a pilot scale co-disposal unit;
- test and optimize the process at the pilot scale.

The laboratory tests for this study included batch leaching (beaker) tests to determine the mass of fly ash required to neutralise the AMD. Fly ash was added in different proportions to a given volume (500 ml) of AMD (solid:liquid ratios from 1:1 to 1:20), and the pH and electrical conductivity of each mixture measured at regular time intervals. The solid and liquid phases were separated by filtration after reaching a stable pH, and the liquid analysed by ICP and ion chromatography methods.

The results showed the effectiveness of the ash in neutralising the acidity of the mine water, and indicated an optimum solid:liquid ratio of 1:3. The concentrations of Al and SO$_4$ in solution also decreased, and, if the suspension was aerated allowing it to be oxidised to Fe$^{3+}$, iron was also precipitated from solution.

The pilot scale mixer consisted of a 250 litre turbulator/aerator unit, with a slightly conical base to allow segregation of the resulting sludge from the liquid. Testing using this facility indicated that a solid:liquid ratio of 1:4 was effective in removing the major contaminants, leaving water of a quality suitable for use in other process applications. Variations in the chemical composition of both the fly ash and the AMD, however, indicated that further optimisation may be needed for full-scale treatment plants. It was suggested that the sludge component could be pumped underground to provide further AMD treatment or to prevent AMD formation, allowing the process to address the environmental risks associated with both AMD pollution and fly ash disposal.

6.2.2. Column Leaching Tests

In a different approach, Reynolds (2005) describes the use of laboratory-scale column tests to assess the feasibility of using particular fly ashes to treat and control AMD in South African open-cut coal mines. Water with pH less than 2 flows through the
surrounding strata from these operations, leaching further heavy metals to add to the water load. Lime treatment of the acid drainage produces a sludge that also contains heavy metals; the sludge is stored, adding to the cost of the treatment process.

Samples of fly ash from different power stations were packed into duplicate columns of four different lengths, and the AMD water from the area passed through all eight columns simultaneously using a constant-head feed system. Water passing out of the columns was collected and analysed at selected time intervals, until the pH of the columns with the coarser ashes dropped below 8, or until the columns containing the finer ashes became blocked due to mineral precipitation. The ash was then sampled from the top, middle and bottom of each column and subjected to XRF and XRD analysis.

The leachates from the coarse ashes showed an initial decrease in dissolved SO$_4$, due to precipitation of gypsum in the columns as part of the acid neutralization reaction. In the longer columns the gypsum remained in place and leached SO$_4$ remained low, but in the shorter columns the concentration of dissolved SO$_4$ in the leachates increased after this initial decrease, as the pH of the leachate dropped and the gypsum became soluble.

The concentration of a number of other elements in the leachate also decreased during the experiments, suggesting precipitation from the AMD by contact with the ash. Elements that were reduced in concentration included Be, Cd, Co, Pb, Ni and Zn, as well as Al, Fe and Mn. Cr and Cu showed a more variable behaviour, typically increasing in the leachates and then decreasing, while B appeared to remain fairly mobile throughout the leaching experiments.

### 6.3. Drainage Control in Mining Operations

Depending on the relation between the mine workings and the regional groundwater system, coal mining may significantly alter the hydrogeology of the area in and around the site. As well as open-cut excavations, the interaction of shafts, utility boreholes, subsidence fractures and other openings associated with underground mines may significantly alter subsurface water flows, even after mining has ceased and the ground surface returned to other land use. Although the surrounding strata may be relatively impermeable, mine openings and underground goaf areas may act as groundwater conduits, effectively representing aquifers of infinite transmissivity. In cases where the water table is lowered and acid-generating (pyritic) rocks are exposed to oxidising conditions, waters with low pH may develop and spread rapidly, leading to a range of acid mine drainage problems. Groundwater discharge from active or, perhaps more significantly, from abandoned mines in such circumstances may also give rise to extensive contamination of streams and other surface waters, as well as affecting the subsurface waters of the region.

Reeves et al. (2005), for example, describe alterations to the regional hydrogeology by abandoned underground workings in western Maryland, USA, where mine openings have intercepted and channelled groundwater into subsurface areas in which acid waters are generated from pyrite oxidation. Groundwater discharge from the abandoned mine workings in this area contributes to artificially high flow rates in the local streams, and to ground and surface waters that are typically high in acidity. A pilot study, the Winding Ridge Project, was commenced in this area in 1996, to investigate the injection of ash-based grout (pozzolan stabilised material or PSM) into abandoned mine voids as an
impermeable barrier to restore the disturbed hydrogeology of the region. Use of ash in this way served to minimise acid generation through blocking access of oxygen or oxygenated water to the subsurface pyritic material, as well as providing flow barriers that minimised contact between contaminated waters and fresh water supplies.

The flow characteristics of the grout used in the Winding Ridge study, monitored by down-hole cameras, allowed maximum distribution of the material through the mine voids from a minimum number of injection boreholes. Cores collected from filled mine voids up to eight years after injection showed good adhesion and contact between the grout and the mine rock surfaces. Laboratory tests indicated that the grout had maintained a high compressive strength and low permeability, making the ash an excellent substitute for Portland cement in situations where grouting is also used for subsidence reduction and overburden support (see later discussion in this review).

Ash may also be used as a permeability barrier to control water contamination in other types of installations. Shang and Wang (2005), for example, describe the use of fly ash in constructing contaminant barriers for reactive mine tailings, and Nhan et al. (1996) and Pranshanth et al. (2001) describe the use of ash mixed with other components as a barrier material for containment of other landfills, such as might be needed for installations at some mine sites. As well as helping to provide a permeability barrier, the ash in such cases may also serve to immobilise heavy metals and other toxic ions, and possibly to neutralise any acid leachates associated with the impounded waste material (see later discussion).

6.4. Ash Use in Open-cut Mines

Placement of ash and other CCBs as structural fill in open-cuts can provide two different but related environmental and social benefits: reclaiming the mined land for other productive uses in an economically and environmentally sound manner, and eliminating the need for converting otherwise useable lands near power stations for landfills and ash impoundments.

Vorries (2001) indicates that ash placement in surface mines takes place under different conditions to ash placements associated with (US) power station sites. Power station ash disposal sites at which release of toxic leachates have occurred typically have the following characteristics (Figure 7):

- geographic placement on a flood plain;
- a geologic setting of alluvial sand and gravel, usually close to a river;
- groundwater that is plentiful and of high quality;
- placement of different types of ash materials (fly ash, bottom ash etc) as a wet slurry without any chemical characterisation of the material;
- reclamation using a shallow layer of fill over the ash, which is then revegetated.

By contrast, placement at (US) open-cut mine sites (Figure 6) is characterised by:

- geographic placement in an upland location;
- a geologic setting of sandstone, shale and other rocks, with an impermeable claystone commonly below the lowest coal seam that was mined;
- groundwater that is limited and of poor quality;
- only CCBs that are tested for leachates and approved under SMCRA regulations are allowed to be placed on the site;
• reclamation is accomplished by a thick layer of spoil over the area, which is in turn covered by topsoil and revegetated.

![Diagram of reclamation process](image)

**Figure 7**: Schematic cross sections showing placement of ash (CCBs) in a river-side power station emplacement (top) and within the spoil pile at an open-cut mine site (bottom); Vorries, 2001.

Murarka (2001) suggests that several million tonnes of CCBs could be used annually in the USA for mine-filling operations, but like other authors notes that perceptions and lack of reliable scientific data still create obstacles to increasing the use of ash in this way, or even to maintaining the practice at current levels. As an example, Murarka (2001) provides a case study of the use of ash as structural fill for an open-cut operation in Indiana (the Universal Mine), at which a total of over 1.5 Mt of ash were successfully emplaced between 1989 and 2001 (Figure 8).

Filling of this particular pit by coal ash has resulted in improvements to the AMD water quality over a 13 year period, neutralising the acidic pH, increasing alkalinity, and decreasing Mn, Fe and SO4 concentrations in the mine water. The ash has, however, contributed to increases in boron and chloride concentrations. Although some of the findings are disputed by Norris (2004), many of the environmentally significant trace metals such as Ba, Cr, Cd, Cu, Pb, Hg, Ni, Se and Ag show no signs of leaching or impacting on the groundwater; As also appears not to have impacted on the down-gradient ground or surface water, despite some indications of leaching from field and laboratory tests.

Branam et al. (1999) describe a comprehensive demonstration project to test the use of ash as mine fill in another open-cut in Indiana (Midwestern Mine site). Before reclamation the groundwater at the site was contaminated by waters from highwall lakes and preparation refuse deposits, and acidic, metal-rich runoff prevented vegetation growth and contributed to erosion and deep gullying at the ground surface. A blend of bottom ash and
fly ash was used as fill material, with a mixture of FGD sludge, fly ash and lime used as a capping material.

Laboratory leaching tests carried out on the ash materials, using 18-hour and 30-day test routines, suggested that trace elements in the ashes used were relatively immobile, but even so it was noted that ambient conditions at the site cannot be precisely duplicated in the laboratory. Groundwater quality was monitored before and after reclamation at sites that documented the effects of the ash on the hydrological system.

A number of environmentally-significant trace elements, such as As, Cd, Cr, Cu, Pb and Ni, were found to be most abundant in the acid waters near the preparation refuse, and were probably derived from these sources rather than from ash emplacement. These elements decreased in abundance in waters with more neutral pH conditions. Boron and molybdenum, however, increased dramatically after reclamation, indicating that they were derived from the ash instead. Molybdenum was found to co-precipitate with iron and thus decrease rapidly in abundance away from the ash source, but boron, which is soluble over a wide pH range, appears to be widely dispersed in the groundwater system.

![Figure 8: Cross section of southern part of the Universal Mine site in Indiana (Murarka, 2001), showing placement of ash in relation to spoil, alluvium and the water table (potentiometric surface).](image)

Perhaps offering a better parallel to conditions in Australian coal mines, ash has also been used as a backfill material in open-cut coal mines that are not associated with acid water conditions. These include a number of mines in the western USA (e.g. Koehler, 2002; Luther et al., 2005), as well as non-coal mine and quarry operations in environmentally sensitive areas in other countries (Brown et al., 1976). A number of issues concerning ash characteristics and site geology need to be addressed in such proposals, including the groundwater characteristics and the relation of the ash emplacement sites to other mine materials on the site and to the subsurface water flow (Young, 2002).
6.4.1. Trapper Mine, Colorado

Koehler (2002) describes the use of CCPs as backfill in selected areas at the Trapper Mine in north-western Colorado, where fly ash, bottom ash and FGD material (scrubber sludge) from combustion of low-sulphur coal have been used as part of the void infilling program since 1984. Investigations prior to accepting the ash as part of the program included a thorough assessment of the hydrogeological setting of the mine and adjacent areas with particular emphasis on groundwater hydrology and water quality, including definition of the overall water balance for the site.

Comprehensive evaluations were undertaken to define the relevant physical and chemical characteristics of the coal, fly ash, bottom ash and scrubber sludge, and also of the various Trapper Mine overburden materials. Laboratory studies were carried out to characterise the chemical composition of the expected leachates, and to identify the attenuation patterns for key constituents resulting from the exposure of the CCB leachates to mine overburden and undisturbed rock strata. The influences and effects of various CCB placement options within the mined area (pit bottom, intermediate bench or spoils trough) on leachate development were also examined.

Findings of the study included:

- The CCBs to be used were non-toxic/non-hazardous materials, and not subject to regulation under RCRA;
- Infiltration and percolation rates at the mine are typically quite low, and there is an associated low potential for CCB leachate development to occur;
- The permeabilities of the mine spoil tend to exceed the permeabilities exhibited by the CCBs; therefore, percolating waters moving through the soil/spoil profile should tend to preferentially move around rather than through the CCB placements;
- Unattenuated CCB leachates were found to have concentrations of Al, Ba, Cr, B and Mo exceeding recommended drinking water and/or agricultural water quality standards; Trapper Mine spoils, however, should consistently attenuate the concentrations of these constituents to acceptable levels;
- No direct hydrologic connection was identified between the coal bearing stratigraphic unit and the adjacent Yampa River, so that the strata to be disturbed by coal mining and CCB placement were hydrologically isolated from the river system.

On the basis of this study it was concluded that selective mine placement of fly ash, bottom ash, and scrubber sludge at the mine was unlikely to produce groundwater contamination. The primary reasons for this conclusion were the minimal infiltration characteristics prevalent at the site, the moisture storage capacities of the overburden materials and the related influence on water balance, the relative impermeability of the CCBs as compared to the spoil materials, and the attenuating influence of the Trapper Mine overburden materials on the CCB leachates.
6.4.2. San Juan Mine, New Mexico

Luther et al. (2005) indicate that fly ash, bottom ash and FGD sludge have been emplaced as backfill in selected parts of the San Juan Mine, located in an arid region of New Mexico with no perennial streams and an average annual rainfall of around 250 mm. The regional groundwater in this area is very saline, with total dissolved solids (TDS) typically exceeding 10,000 mg/l.

Previously-mined areas are filled with coal combustion products and mine spoil to return the land to approximately the original surface configuration. Approximately 2.7 Mt of CCPs (around 70% fly ash, 15% bottom ash and 15% FGD sludge) are placed into the pit annually as part of this reclamation process, representing about 3% of the total volume of material handled at the mine site. The CCPs are placed in discontinuous pockets and layers, surrounded by and commonly interbedded with low permeability spoil materials. The CCPs are buried beneath and average of 3 m (10 feet) of other backfill material after final placement.

The CCPs used at the San Juan Mine are very alkaline (pH 7.4 to 12) and have low salinity (EC 0.15 to 3.18 dS.m\(^{-1}\)). Laboratory tests show that the CCPs have a low permeability, with saturated hydraulic conductivity values of 2.3 x 10\(^{-7}\) cm.sec\(^{-1}\), or about 7.3 cm per year. The mine overburden materials are dominated by sodium-saturated smectitic clays with secondary accumulations of sulphate and carbonate salts. They are relatively saline (EC 4 to 8 dS.m\(^{-1}\)), sodic (SAR 15 to 60) and alkaline (pH 7.2 to 9.5), and are essentially impermeable, with a saturated hydraulic conductivity of <10\(^{-8}\) cm.sec\(^{-1}\))

The concentrations of trace elements in the fly ash, bottom ash and overburden rocks at the San Juan Mine are similar, with the ash having lower concentrations of some elements than the overburden materials. Leachability testing was carried out to help identify the potential mobility of key elements, and to provide data for predicting the hydrological consequences of using the CCPs in the mine backfill. Testing included leaching of overburden (backfill) materials and of backfill-plus-CCP samples with a composite of groundwater from four wells drilled into the main coal seam. The likely impact of the CCPs on groundwater quality was evaluated by analysing the water before and after equilibration with the respective solid components. Because water from the backfill is expected to travel through adjacent areas of coal mined-out by underground operations, and then eventually through the subsurface coal seam itself, leachates generated from laboratory equilibrium between the groundwater, backfill and CCPs were also equilibrated with samples of coal from the relevant seam. The resulting solutions were analysed and compared to the backfill-CCP leachates, to assess the coal’s attenuation potential.

The laboratory studies and modelling process have indicated that no significant degradation of the groundwater is likely to arise from the use of ash at this mine site. The prediction is supported by groundwater monitoring data from 17 locations in and around the mine, which also show no impact from the process.

6.4.3. Navajo Mine, New Mexico

Young (2002) describes the placement of ash and other CCPs at the Navajo Mine, also located in the San Juan Basin of New Mexico. Key features of the program include:
• Ash is generally placed only in inactive pits that have been completely mined out. A typical ash disposal area is trapezoidal in cross-section, with the top width averaging 120 m (400 feet), the bottom width 45 m (150 feet), and a depth of up to 40 m (120 feet). This arrangement results in the ash being restricted to relatively small areas within the mine, which facilitates long-term solutions to reclamation design and planning issues associated with minimizing potential exposure of the ash;

• Ash must be covered by a minimum of 3 m (10 feet) of spoil material, plus any required spoil mitigation material, plus the required topsoil thickness. Average ash cover thickness is on the order of 3.6 m (12 feet);

• The AOC (approximate original contours, the reclaimed lands configuration) surrounding all ash disposal areas is designed to have positive drainage away from the ash and avoid any puddling or other collection of water above or adjacent to disposal areas;

• All post-mining drainages that intersect an ash disposal area must flow across the ash disposal area at approximately right angles to the long axis of the disposal site, to minimize potential infiltration of surface waters into the ash;

• Pit-run spoil has a low permeability of $10^{-6}$ cm.sec$^{-1}$, which minimises vertical infiltration of surface water. After mining is completed, the pit floor will be on the top of a shale/mudstone parting with low permeability ($10^{-7}$ cm.sec$^{-1}$, comparable to many commercial grade liners). The surrounding spoils will be a mixture of sandstones, mudstones, and shales, with permeability around $10^{-6}$ cm.sec$^{-1}$;

• Active ash disposal areas must be regularly plated (with spoil material) to cover the surface and minimize fugitive dust;

• Ash disposal areas are revegetated to support the post-mine land use of grazing; lands previously used for ash disposal have met revegetation success criteria to qualify for an OSM Termination of Jurisdiction. Relevant studies included determination of an appropriate thickness of cover (spoil) over the ash to prevent plant roots from contacting the CCPs, and sampling of plant tissue, which confirmed that metals were not becoming concentrated in the associated vegetation;

• Disturbed areas are also subject to a bond for 10 years after the final seeding process.

The concentrations of key trace elements in the CCPs and the spoil disposed of at the Navajo Mine are presented in Table 9. The only notable differences between the ash and the spoil are that the fly ash has elevated concentrations of Ba, and slightly higher concentrations of Se and Cr relative to the spoil material. Although not listed, concentrations of boron also are also slightly higher in the ash. Both bottom ash and fly ash have lower concentrations of sulphate, Na, and Ca when compared to the spoil.

Leachate studies suggest that concentrations of dissolved boron and selenium slightly increased when surface waters from the area are leached through the fly ash. However, the boron concentration declined when the water was leached through a mixture of ash and spoil, and the selenium concentrations from the ash were similar to the selenium concentrations in leachate produced by the spoil alone. The iron concentration in both surface and groundwater decreased following leaching through spoil, CCP, or a mixture of the two. Leachate produced from mixtures of ash and spoil had a lower TDS.
concentration and lower trace metal concentrations than natural groundwater from the main coal seams.

Trace metal concentrations are similar for all the leachates produced, with the exception of fly ash alone, which showed an increase in boron concentration. However, boron concentrations in groundwater leached through a mixture of ash and spoil are similar to the original B concentration in the groundwater. The leaching study predicted that if the CCB should contact the groundwater, regardless of whether the water is derived from coal seam groundwater or infiltrating surface water, no degradation to post-mine groundwater should occur. The study also concluded that the spoils are capable of retarding the movement of metals in percolating water; specifically, levels Ba, Fe, Se, and Pb decreased in some cases. Geochemical processes thought to be responsible for this are adsorption, the high cation-exchange-capacity (CEC) of the spoil, and precipitation of material from solution.

Table 9: Concentrations (mg/l) of selected trace elements in ash and spoil at the Navajo Mine, New Mexico (Young, 2002).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ash</th>
<th>Spoil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>8.5</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Arsenic</td>
<td>8.65</td>
<td>13.9</td>
</tr>
<tr>
<td>Barium</td>
<td>746</td>
<td>204</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.6</td>
<td>1.32</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.3</td>
<td>1.14</td>
</tr>
<tr>
<td>Chromium</td>
<td>6</td>
<td>2.8</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1.7</td>
<td>7.6</td>
</tr>
<tr>
<td>Copper</td>
<td>9</td>
<td>9.4</td>
</tr>
<tr>
<td>Lead</td>
<td>3</td>
<td>38.2</td>
</tr>
<tr>
<td>Manganese</td>
<td>60.1</td>
<td>284</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.11</td>
<td>0.26</td>
</tr>
<tr>
<td>Nickel</td>
<td>2.5</td>
<td>11</td>
</tr>
<tr>
<td>Selenium</td>
<td>4.35</td>
<td>0.6</td>
</tr>
<tr>
<td>Silver</td>
<td>0</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Thallium</td>
<td>0</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Zinc</td>
<td>14.5</td>
<td>65.4</td>
</tr>
</tbody>
</table>

6.4.5. Ash Use in Australian Open-cut Mines

The Macquarie Generation web site describes a special rehabilitation project (Figure 9), commenced in 1996, that uses fly ash from Bayswater Power Station to fill open-cut mine voids at nearby Ravensworth (http://www.macgen.com.au/environment/overview.htm). The mine voids are being progressively filled with ash, covered with topsoil and re-vegetated, and the project has been followed through to the point where the land can now be returned to grazing.
The topsoil used in the project was made from ash and other recycled waste products. A Sydney-based company, Bio-Recycle, manufactured its soil conditioner Mine-Mix™ on-site using biosolids from the Hunter Water Corporation along with coal ash, lime and gypsum. A ready supply of biosolids is available, and Macquarie Generation produces the other three ingredients in the normal course of operations. The company produces up to two million tonnes of ash per year, and the lime and gypsum are by-products of Bayswater’s water treatment system. Sales of 60,561 tonnes of fly ash and 5,154 tonnes of bottom ash were reported by Macquarie Generation for 2002-2003, along with 475 tonnes of lime and 2,067 tonnes of gypsum.

6.5. Ash Use in Underground Mines

Placement of backfill is common practice in underground metalliferous mines, mainly for ground control in conjunction with stoping operations (Potvin et al., 2005). Backfilling is less common in underground coal mines, but has nevertheless been investigated in recent years as a basis for ground control or for reducing subsidence and hence increasing the recovery of in-situ coal resources. Grice et al. (1999), for example, describe the use of an ash-based backfill to help confine the roof and rib of development headings under the stresses associated with an advancing longwall face, providing increased coal recovery from an otherwise difficult area in the Wambo mine, New South Wales. Holmquist et al. (2003) describe the use of ash-based grout to reduce subsidence impacts associated with underground coal mines in Colorado and Wyoming, and Palarski (1998) describes backfilling of Polish longwalls with coal tailings and aggregate to minimise goaf settlement and enable thick seam extraction by multiple slice methods. Grice et al. (1999) also describe a longwall mine in Germany in which municipal and industrial wastes are stowed to reduce subsidence effects, with the cost of placement offset by fees to perform the waste disposal service.

Research by the Australian coal industry on backfill in underground mines is mainly focused on geotechnical aspects of the fill material and the technical feasibility of its emplacement. Recent studies in this regard include ACARP Project C7033, *Utilising Fly Ash Paste Backfill*, which investigated the properties of dense fly ash pastes rather than more dilute slurries as a backfilling medium, and Project C6014, *Highwall Mining*
Backfill, which investigated the use of cement-stabilised coal preparation wastes as backfill to increase recoveries from highwall mining operations. Project C12019, Subsidence Control using Overburden Grout Injection Technology, is currently investigating the feasibility of injecting fly ash into overburden strata through boreholes to reduce subsidence over longwall areas. ACARP documentation indicates that a similar process has been used successfully in China since the mid 1990s, with benefits to mines located relatively close to appropriate ash sources.

Because of the way in which it is used, and the benefits gained from its introduction, the most critical factors associated with the use of ash in ground support and subsidence control are in most cases the geotechnical properties of the backfill material. These include the flowability, density, porosity, abrasiveness and strength, as well as the pozzolanic or cementitious properties of the mix. Indeed, many studies of ash and ash-bearing fills in Australian underground mines, including the comprehensive review by Potvin et al. (2005), are strongly focused on such properties, and either do not consider the chemical interaction with mine water and the surrounding environment or provide only a brief mention of any assessments other than those involving the geotechnical characteristics of the fill material.

As well as the geotechnical factors, however, chemical interactions between ash, mine rock and water may also be significant to such backfill programs (e.g. Singh and Paul, 2001), and are equally necessary if regulatory, industry or community concerns that introduction of backfill may also have an impact on the associated groundwater quality are to be addressed. They are also significant in evaluating the potential for corrosion of metal pipes in backfill and other ash handling operations (Loadwick, undated).

6.5.1 Wambo Colliery, New South Wales

Grice et al. (1999) describe the use of an ash-based backfill to stabilise openings that had previously been driven in an area planned for longwall mining at Wambo Colliery, in the Hunter Coalfield of New South Wales. The openings, a series of stub headings that had been driven ten years earlier by bord and pillar techniques, extended into an otherwise virgin block of coal. If not stabilised their presence would have provided a major disruption to continuity of the longwall extraction process, resulting in a significant loss of both coal resources and production time.

Alternatives investigated in this instance were:

- Mining up to a point near the stub headings and then re-establishing mining on the other side;
- Re-supporting the mined-out openings with roof-bolts, cable-bolts and fibre-crib supports and then mining through the specially supported area;
- Placing a low strength backfill material, to provide effective confinement of the coal pillars and then mining through the backfilled area.

Geotechnical and economic studies showed that the backfill option was the most feasible, and the company applied for a variation to the approval conditions for mining the block, including a full environmental assessment and a full risk and hazard analysis.

The backfill in this instance provided confinement for the roof and ribs (sides) of the previously-driven openings, when they were ultimately subjected to the loadings imposed
by the advancing longwall face. A cemented sand backfill was used, with a target unconfined compressive strength of 4 MPa and a modulus of 500 MPa after 28 days. The backfill also had to have appropriate flow properties at a high slurry density, to enable placement through a borehole into the mine workings, and be able to build a flat surface after placement to ensure a near-tight contact with the roof strata.

Fly ash was used as a partial cement replacement, acting both as a plasticiser and as a binding material. A mixture of sand, Portland cement and fly ash was used, with a slurry density of 85% solids. The materials were mixed on site and pumped underground into the prepared and barricaded-off mine openings. A total of 12,000 m³ of fill was injected in this way over a two-month period, including a two-week wet-weather delay.

After placement and curing, the backfilled area was successfully mined through. The fill formed a homogeneous, unjointed mass, clearly visible against the coal, and was effectively removed in the coal preparation process. Some abrasiveness was encountered from the sand grains in pumping the fill and also in mining through the material; but replacement of the sand by another material was considered to be a less economic alternative in this particular instance.

Backfilling of development headings ahead of longwall mining has also been successfully carried out at other mine sites, including Cyprus Emerald Mine (Chen et al., 1997) and Foidel Creek Mine (Seymour et al., 1998) in the USA. Other applications for this technique include the pre-mining and backfilling of stone dykes in longwall panels. Palarski (1998) also describes backfilling practices in the Polish mining industry, where longwalls are routinely filled with coal tailings and aggregate to minimise goaf settlement and enable extraction of thick coal seams.

6.5.2 Peabody #10 Mine, Illinois

Singh and Paul (2001) describe a series of environmental investigations associated with injection of coal combustion products into an underground coal mine in southern Illinois, USA, as a mechanism for subsidence control. Two different mixtures were evaluated: a pneumatically-injected blend of natural pH 12.26, consisting of 80% fly ash and 20% bed ash from a fluidised-bed combustion plant and a hydraulically-injected paste of pH 11.10, made up of a type F fly ash from pulverised coal combustion (40%) combined with a sulphate-rich scrubber sludge (55%) and lime water (5%).

The leaching characteristics of these mixtures, and also of the individual mixture components, were evaluated using the US-EPA toxicity characteristic leaching procedure (TCLP – US-EPA Procedure No 1311) with a buffered acid medium, and also the ASTM column leaching procedure (ASTM D 4874). In the latter test, one pore volume of distilled water was forced through a packed column of the solid material in a saturated up-flow mode. The tests were conducted in a nitrogen atmosphere, to represent on-site leaching under oxygen-poor conditions; these could not be modelled in the TCLP (shake-type) tests. Testing was carried out over 16 days, with leachates collected at appropriate intervals for analysis. Leachates from both tests were analysed for pH, electrical conductivity, chlorine and fluorine using potentiometric techniques, and then acidified with nitric acid and analysed by atomic absorption spectrometry (AAS) and inductively-coupled plasma (ICP) emission techniques. The calcium carbonate equivalent (CCE) of
the mixtures and the individual components was also determined using an automatic titration procedure.

The coal combustion products in this case did not yield significant concentrations of regulated cations (heavy or toxic metals), when assessed by the TCLP procedure. However, the leachates from the materials were expected to be high in dissolved solids (especially Na and Ca) and sulphates, and high concentrations of boron and chloride were also expected to be leached out in the early stages of the emplacement process. The Peabody #10 mine site is nevertheless surrounded by low-permeability brine-bearing rock units, and as such is effectively isolated from any potentially useful ground and surface water resources. For this reason no leachate problems were considered likely at the emplacement site.

### 6.5.3. Backfilling in South African Coal Mines

Ilgner (2000) provides a history of ash backfill in South African underground coal mines, starting with hydraulic placement to stabilise coal pillars at Koornfontein Colliery, in the Witbank area, in 1963. Another large-scale backfilling operation commences at Springfield Colliery in 1973, with about 3,000 tonnes of ash from Grootvlei Power Station being placed on a daily basis. Re-opening of a previously ash-filled roadway some 35 years later showed that the ash, although still water-saturated, has consolidated to a compact fill; it had also maintained good lateral contact with the coal pillars, resulting in sufficient confinement to prevent weathering or dilation of the coal after the fill had been placed.

Another operation, commenced in 1994, used ash-fill injected through boreholes to stabilise a section of a major national road. No collapses have occurred in the filled areas, although similar unfilled areas have collapsed. On-going monitoring of the underground water quality indicates that the ash-fill operation is environmentally friendly.

Underground ash-filling in South African mines has resulted in additional recovery of coal resources on a site-specific basis. However, excessive quantities of drainage water, operational problems, working out of coal reserves and closure of nearby power stations has resulted in the termination of those ash-fill operations. Recent concerns, such as the increasing occurrence of subsidence over mined-out areas and the limited remaining life of some coal mines, have led to a re-evaluation of the benefits derived from ash filling.

Despite the decline in the extent of ash-filling, backfill technology has advanced significantly in South Africa since the late 1980s, and fast-draining tailings are placed daily as un-cemented backfill in operations well integrated with the mining cycle. Backfill distribution systems based on sophisticated computer modelling and a thorough understanding of the backfill rheology are now being designed. An integrated approach has been suggested to maximise the overall cost/benefits of underground ash filling to both power stations and coal mines (Figure 10).
The ashes from South African power stations have different physical properties, which affect their hydraulic transportation and underground drainage behaviour after placement as mine fill. Several power stations, however, produce ash with inherent pozzolanic potential, which can provide sufficient lateral confinement to increase the load-bearing capacity of coal pillars and maximise extraction of the in-situ coal resources.

According to Ilgner (2000), relevant ash properties for consideration include:

**Proportion of Ultra-fine (<0.01 mm) Particles:**

The proportion of particles coarser than 0.01 mm varies between 15 and 30% for South African ashes (i.e. <0.01 mm ranges from 70 to 85%). The materials with a higher proportion of ultra-fine material have lower permeabilities than those with lesser proportions of ultra-fines, requiring longer periods (of the order of weeks) for drainage and strength development, compared to fill based for example on mine tailings.

**Maximum Practical Slurry Density:**

The viscosity of ash-water slurries increases with slurry density, which impacts in turn on the relative pipeline pressure loss in pumping operations. Significant differences have been noted for different South African fly ashes in the density at which the increase in pipeline pressure loss takes place (Figure 11), possibly as a result of differences in feed coal preparation, burner operating temperature and ash collection methods. Data such as that in Figure 11 provide a basis for designing practical ash distribution systems for mine backfill, while maintaining the highest possible slurry density.
Drainage Water Quantities:

The amount of water expected to drain out of the ash emplacement, per tonne of ash placed, is also a significant issue for consideration. This depends in part on the slurry density and the in-situ porosity of the consolidated ash emplacement.

Ash Mineralogy:

Ilgner (2000) indicates that the pozzolanic properties of South African ashes are related to the ash mineralogy (as determined by XRD techniques) and texture (mode of mineral occurrence), especially the proportion of non-crystalline or glassy components. The glass in South African ashes occurs mainly as different-sized spherules, but a certain percentage of the glass may occur instead as small coatings on other components. The glass coatings tend to prevent the inherent pozzolanic reactions in the ash, and as a result a pozzolan index (PI) has been developed for South African ashes calculated as follows:

\[
PI = \frac{(\text{glass spherules } \%) \times (100 - \text{coating } \%)}{1,000}
\]

Table 10 ranks a series of South African ashes in terms of this PI value, showing also the link between glass content and pozzolanic properties. The Matla ash identified in this table is regarded as particularly suited for underground fill, due to a relatively high slurry density suitable for hydraulic transportation, a relatively small percentage of drainage water, and a high potential as a pozzolanic cement extender.

Other aspects for consideration include the stress-strain relationships for laboratory-consolidated ash samples and the interaction of the ash with the mine water and ground water through processes such as AMD neutralisation. A summary of the various factors involved in design and implementation of ash-based backfill projects is given in Figure 12.
Table 10: Relative ranking of pozzolan potential for South African fly ashes (Ilgener, 2000)

<table>
<thead>
<tr>
<th>Ash</th>
<th>Glass %</th>
<th>Coated %</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matla</td>
<td>60</td>
<td>30</td>
<td>4.20</td>
</tr>
<tr>
<td>Lethabo</td>
<td>60</td>
<td>50</td>
<td>3.00</td>
</tr>
<tr>
<td>Kriel</td>
<td>40</td>
<td>60</td>
<td>1.60</td>
</tr>
<tr>
<td>Kendal</td>
<td>60</td>
<td>75</td>
<td>1.50</td>
</tr>
<tr>
<td>Arnot</td>
<td>50</td>
<td>75</td>
<td>1.25</td>
</tr>
<tr>
<td>Duvha</td>
<td>40</td>
<td>70</td>
<td>1.20</td>
</tr>
<tr>
<td>Tutuka</td>
<td>40</td>
<td>80</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Figure 12: Criteria for backfill system design in underground coal mines (Ilgener, 2000).

6.6 Use of Ash in Coal Seam Fire Control

In-situ combustion of coal seams may occur in underground or open-cut operations (mine fires), and also near natural outcrops or in stockpiles and refuse dumps, as a result of the heat generated by interaction of the coal with oxygen from the atmosphere. A number of environmental and health hazards may arise in association with such fires, through processes such as surface subsidence, air and water pollution, destruction of surface vegetation or structures, and loss of otherwise useable coal resources. Such fires may break out at any stage of the mining cycle, ranging before any mining commences in the case of outcrop fires to after the mine has been decommissioned and the land returned to other uses.

A report by Kim and Chaiken (1993) suggests that a total of 99 mine fires were active in the USA in the early 1990s, covering an area of some 21 km². This represents a significant reduction from the 261 recorded in 1977 (Johnson and Miller, 1979), but still involves a potential rehabilitation cost of $US741 million, almost ten times the 1977 estimate. Although no comparable figures are available for Australia, McNally (1997) describes several active mine fires in the Newcastle Coalfield of the Sydney Basin, and indicates that additional fires are burning in the Western Coalfield of NSW and the
Ipswich Coalfield of Queensland. The Burning Mountain, near Wingen in the Upper Hunter region, provides a natural example of a long-lived in-situ coal seam fire extending from outcrop over a significant land area.

Colaizzi (2004) describes the use of a cellular, foam-based grout to mitigate coal fires under different conditions, including fire prevention, control and extinguishment. The grout is made up of Portland cement, fly ash, aggregates and special foams, providing a highly flowable, heat-resistant material that can simultaneously address the three elements associated with a fire: fuel, oxygen and heat. Fires can be prevented by spraying the material on the exposed coal surface (e.g. after exposure in open-cut mines), or by injection of the grout into cracks, vents and cut-off trenches to stall or prevent continued fire growth. Active fires can be extinguished by injecting the grout directly into the fire zone, air intakes or exhausts.

The material described by Colaizzi (2004), marketed as Thermocell, is composed of sand, cement, water and a high proportion of fly ash, to which is added a quantity of air-entraining foam. It is reported to be capable of direct application to a red-hot coal fire without steam explosions or grout flash set. Once in contact with the fire the grout encapsulates the burning material, removing the heat and fuel. It also fills the void spaces and passages, thereby sealing the fire from its oxygen source.

Injection of an ash-bearing grout provides a safer and lower-cost alternative to other means of fire control, such as excavation of the burning material. It also causes less disruption to the surrounding environment and comes into effect more quickly. Incorporation of ash into the grout, moreover, provides a mechanism for beneficial use of a waste material associated with the main product of the mining process.

McNally (1997) describes the use of different fire suppression techniques in the underground mines of the Newcastle area, including surface sealing, flooding and quenching, and the use fly ash and other materials as bulk fill for air exclusion purposes. Fly ash is an attractive material for use as bulk fill, especially in the Newcastle area, since it has a high fluidity and is readily available from nearby power stations and associated lagoon emplacements. The fly ash may be injected wet or dry, although pneumatic stowing allows its spread to be more controlled and hence is the more favoured method at present. Ash may also be injected as rock paste, represented by a viscous, self-cementing slurry of fly ash, chitter (washery refuse or other granulated rock) and lime. McNally (1997) notes that trials have been carried out at Rhondda Colliery, near Fassifern, to evaluate the use of fly ash for fire suppression. The ash not only blocks airways and creates fireproof barriers, but also retains water, even on steep grades, assisting fire control also by flooding techniques. Heeley and Shirtley (2001) further confirm that a significant quantity of fly ash is being used in the Newcastle area for this purpose, recovered from the ash pond at Eraring Power Station and trucked to the mine site as back-load from coal deliveries.

6.7 Ash as a Contaminant Barrier for Mine Tailings and Similar Materials

Strategically-placed barrier materials may be needed to reduce the escape of water-borne contaminants from potentially toxic mine products, such as reactive, possibly acid-generating preparation tailings and also municipal solid waste (MSW) materials, into the
surface and subsurface water systems. Barriers used for this purpose typically include compacted clay soils, geomembranes and combinations of the two. As well as escape of contaminated waters, such sealing and covering layers are also intended to inhibit the influx of atmospheric oxygen and/or rainwater, which might otherwise generate acid-forming reactions in the materials concerned.

Several authors, including Nhan et al. (1996) and Shang and Wang (2005), have suggested that incorporation of fly ash into such barrier systems may provide a basis for immobilising some of the otherwise soluble contaminants (e.g. heavy metals) released from mine tailings emplacements. Alkaline fly ash, in particular, may act not only to neutralise acid drainage in such cases, but also potentially fix some of the contaminants into the solid phase through ion exchange or precipitation processes.

Studies by Nhan et al. (1996) indicated that a mixture of fly ash, lime kiln dust and calcium bentonite in a ratio of 7:2:1 could be used to produce a liner that was not only of very low permeability (4.3 x 10^{-8} m sec^{-1}) but that also had the capability of reducing the concentration of dissolved metals in the leachate passing through. In other studies, Mollamahmutoglu and Yilmaz (2001) indicate that an optimum hydraulic conductivity is achieved with a bentonite:ash mass ratio of 1:5. Pranshanth et al. (2001) note that pozzolanic fly ashes encourage the formation of gelatinous compounds, which serve to block the void spaces and provide the main reason for the decrease in permeability with this type of application.

Shang and Wang (2005) provide details of the assessment of different fly ashes for use in contaminant barrier applications, based on studies of ashes from Canadian power stations. The engineering properties of the fly ashes were investigated, followed by laboratory-based column leaching tests with water and with relevant AMD permeation. The column leaching tests were used for a number of purposes, including:

- Measurement of the breakthrough hydraulic gradient, or the hydraulic gradient required to generate seepage flow in the compacted fly ash samples;
- Measurement of the seepage flow and hence calculation of the hydraulic conductivity of compacted fly ash samples of known density;
- Collection and analysis of leachate permeated through the fly ash, as well as monitoring of chemical changes in the leachate over time.

It was found in this particular study that the breakthrough hydraulic gradient required for seepage of AMD through the fly ash was up to 10 times that required for water alone. When permeated with acid drainage of pH 3.8, the compacted fly ash demonstrated a decrease by more than two orders of magnitude in hydraulic conductivity, the effluent from the compacted ash remained alkaline after more than 12 pore volumes of seepage flow, and the concentrations of regulated trace elements were well below the levels set by the local regulating authority.

Nhan et al. (1996) investigated the behaviour of a barrier material made up of the fly ash, lime kiln dust and bentonite barrier described above when in contact with synthetic MSW leachate, partly to determine whether the leachate might attack the solid matrix of the barrier and degrade its porosity. The study was also intended to determine the ability of the barrier to attenuate metal ion contaminants in the leachate, and hence to estimate the life of the barrier and its suitability for long-term application. Test specimens of the barrier material were prepared to a density found from other studies as being optimum for barrier performance, and the samples cured after compaction by exposure to water-
saturated air for one day followed by immersion in deionised water for seven days. The cured specimens were then tested in a constant pressure-head permeameter apparatus with an upward one-directional flow, with the effluent leachate collected for analysis. The hydraulic conductivity and effluent pH with deionised water were also determined for each barrier specimen, prior to testing with the synthetic MSW leachate material.

The study concluded that the fly ash barrier appeared to provide an effective chemical barrier for the MSW leachate, and a pilot scale experiment was recommended as the next stage of the assessment process. The principal retarding mechanism in this particular case was thought to have been precipitation of contaminant metals (Fe, Zn, Pb) as hydroxides and/or carbonates. Breakthrough of metal ions occurs after neutralisation of the barrier material by the acidic leachate following dissolution of the precipitated solids, but even so the migrating front of heavy metals was estimated to be 0.1 m in 15 years, assuming an MSW leachate of pH = 6.

7. ASH USE IN MINE SOILS AND REFUSE EMLACEMENTS

The use of fly ash and other coal combustion products to amend and upgrade the properties of different soils for agricultural and/or horticultural purposes represents an area of beneficial use that could potentially accommodate large volumes of ash from coal utilisation in an economically, environmentally and socially acceptable way. As indicated elsewhere in this review, detailed studies of this application are outside the scope of the current CCSD research program.

A part of such activities relevant to the present study, however, is the use of ash for improvement of natural soils, or construction of artificial soils, to enhance mine-site revegetation programs. Indeed, use of ash to enhance revegetation at mine sites may provide an excellent basis to demonstrate the effectiveness of ash usage for more general use in soil applications, and encourage wider acceptance of ash as a soil conditioner by the agricultural and horticultural industries, the regulating authorities and the community in general. For this reason a brief review of issues associated with ash use in soil applications, where interaction with plants as well as with water must be taken into account, is also included as part of this review document.

7.1 Water Retention and Permeability

Due to a combination of the dominance of silt sized particles and the porous nature of the components, addition of coal ash may be used to increase the water-holding capacity and modify the permeability of otherwise unfavourable soils, and hence increase the level of water infiltration and retention and decrease the rate of water loss. Research sponsored by the Ash Development Association of Australia, for example (Pathan et al., 2001; 2002), has shown that ash addition to sandy soils can reduce episodes of moisture deficits and also aid the retention of nutrients such as nitrate, ammonium and phosphorus in the rooting zone, leading to increases in plant yield and a range of associated economic and environmental benefits.

Ash may also be used to increase the porosity and permeability of clay-rich soils, lowering bulk density, providing better water infiltration and increased aeration (Yunusa et al., 2005). Ca in the ash (otherwise added as lime or gypsum) may act as a flocculant,
further increasing porosity/permeability. Porosity and permeability reduction may occur, however, if the ash develops pozzolanic properties in the soil over time (Carlson and Adriano, 1993). The fine particle size may also result in loss of non-coherent ash from unstablisised surfaces due to wind and/or water erosion, providing potential for off-site impacts from ash emplacement. Cementitious ash, on the other hand, may act as a stabilising agent, reducing the ease with which soil erosion might occur (Tishmack et al., 2001).

7.2 Changes in pH and Nutrient Levels

Addition of ash may change the pH of the soil, and hence the mobility of some of the key elements affecting plant growth. Alkaline ash is often used as an amendment (or liming agent) to reduce the acidity of soils with low natural pH values. Research by Killingley et al. (2000), for example, has shown that Ca and Mg in ash are inherently more abundant in alkaline fly ashes, making those elements also more available for plant growth. The overall proportions of Ca and Mg, and hence the potential value of particular ashes in this context, further depend on the mineral matter in the original coal (Ward and French, 2005). Because of the additional presence of other elements, ash is not as effective as agricultural limestone in causing pH change, and greater dosages may need to be added to achieve the required neutralising capacity (Carlson and Adriano, 1993). It may, however, offer substantial cost advantages, at least in areas located near relevant ash sources. Weathered or water-washed ash (e.g. ash from existing ponds) may be less effective than dry fresh ash in producing immediate pH change (Adriano et al., 1980), but because weathered ash may contain carbonate minerals it can also be associated with more stable salinity levels in the soil over the longer term.

Addition of ash may provide chemical nutrients otherwise lacking in soils, including but not restricted to the Ca and Mg mentioned above. This allows the ash to make up deficiencies that might arise due to prolonged weathering processes in natural soils, or to depletion by extended cropping, and ash may thereby further help to promote plant growth. Ash is, however, inherently deficient in nitrogen, which is lost from the coal during combustion. The phosphorus content of coal ash may be variable, and not all of the P in the ash may necessarily be available for plant growth. Phosphorus may be fixed (immobilised) in acid soils, for example, by interaction with elements such as Fe and Al (Mitra et al., 2005). Alternatively, the ash may initially adsorb P from other fertilisers, and then release it gradually as the P levels in the soil become depleted by plant growth (Butler, 1999).

Sulphur (as SO₄) is often abundant in coal ash, and the SO₄ content of some overseas ashes in particular may be comparable to that of gypsum. Potassium, however, is low in most Australian coal ashes. The ash may also be a source of micro-nutrients that are significant for plant growth, including Fe, Cu, Zn and Mn. Jankowski et al. (2004) have shown that the mobility of many such elements is pH sensitive, so that some may be mobilised and some may be immobilised, depending on the soil conditions.

7.3 Essential Elements and Biotoxicity

Many coal ashes contain elements that, if present at high concentrations in mobile form, could have adverse effects on crops, the soil and perhaps groundwater quality (Adriano et
The ash may introduce some elements, such as B, Mo, Se, that are beneficial if not essential at certain concentrations but may become toxic at higher concentration levels. Toxicity due to such elements may be either direct (e.g. kill off the plants) or indirect, with impacts further along the food chain. Indirect pathways include take-up of particular elements in high concentrations by plants, building to levels that may not necessarily be harmful to the plants themselves but could be harmful when the plants are subsequently ingested as food for animals or people (Carlson and Adriano, 1993). Ash-induced toxicity might also include seepage of water from the soil to lakes, mangroves etc, with a resulting impact on fish populations.

Boron and selenium are perhaps the main elements in fly ash that are beneficial at low concentrations but could prove toxic to plants if released in excessive quantities through the soil-water system. A larger fraction of the B than other trace elements in coal ash is typically mobile with exposure to water, partly because the element is relatively volatile in combustion and hence condenses at a relatively late stage to form a coating on the surfaces of the ash particles. At least in Australia, boron also appears to be more abundant in alkaline fly ashes than in acid fly ashes (Jankowski et al., 2004), and is more likely to be released into solution from alkaline fly ashes under soil conditions. The proportion of boron and other potentially toxic elements in ash has also been found to be reduced by leaching and/or weathering of the ash, even with only short-term storage in ash ponds (Ward et al., in preparation). Boron may also be immobilised in some cases by interaction with calcium to form relatively insoluble mineral phases (Hobbs and Reardon, 1999; Zhang and Reardon, 2003). The potential for boron toxicity is nevertheless one of the main technical factors that could limit the use of particular ashes in soil amendment, and thus boron and its mobility often represent one of the main focal points for soil amendment investigations.

As well as increasing the availability of some elements, addition of ash may reduce the heavy metal content of particular soils by dilution, adsorption or precipitation processes. Heavy metal mobility is controlled by the interactions between ash and other soil components (minerals, water, organics). Robinson et al. (2005), for example, have investigated the adsorption and desorption of Cd, Cu and Zn to fly ash as a function of pH and solution concentration, using batch and column leaching tests, as a basis for using ash in a soil amendment at degraded land-sites.

The cation exchange capacity (CEC) for most fly ashes is less than that of a typical clay-bearing soil, but is often high enough to enhance the CEC of sandy soils. This also has an impact on element availability for plant growth. The CEC of ashes may, however, be reduced by sluicing or weathering processes, and an investigation of these effects will again form part of the present work program. Addition of ash can also give rise to increases in soil salinity. Plant response to salinity has been related to the electrical conductivity of either an extract from the in-situ soil or the response of the soil to laboratory leaching tests (Aitken et al., 1984).

7.4 Blending of Ash with other Soil and Mine Materials

Depending on the ash composition and behaviour, blending of ash with other inorganic components (development of an ash–fertiliser blend) may be a cost-effective mechanism for enhancing the usefulness of particular ashes in soil applications (Spark and Swift, 2005). Blends of ash and organic wastes (e.g. municipal waste, farmyard manure, crop
residues, paper sludge) may also be used to provide an integrated nutrient supply for crops such as rice, peanuts and tomatoes, allowing reductions in the cost of chemical fertilisers otherwise required (Hart et al., 2003; Mittra et al., 2005). The chemical fertiliser, ash and organic materials are not substitutes for each other in such circumstances, but have complementary roles.

Synthetic soils may also be developed for use at mine sites (e.g. from preparation refuse, ash and appropriate organic wastes), as an enhancement to or even a substitute for topsoil placement in rehabilitation programs (Daniels et al., 1999; Stewart et al., 2001, Chugh and Balk, 2004; Truter and Rethman, 2005). Along with the use of ash in mine backfill, this could also represent a significant market for coal ash in mine-site applications.

7.4.1 Engineered Mine Soils, Southern Illinois

Chugh and Balk (2004) describe the use of an engineered soil based on fine coal processing waste (~100 mesh), fluidized bed combustion fly ash and animal wastes as a stabilized material suitable for reclamation and vegetation growth. Commercial use of this material will minimize environmental impacts associated with by-product disposal, as well as reduce pond requirements for preparation wastes, landfill space requirements for ash disposal, and runoff from animal wastes into surface and subsurface water supplies.

The developed soil was made up from 75-85% fine coal waste and 3-12% FBC fly ash from a mine and power plant in central Illinois, and 2-7% animal wastes from southern Illinois. The soil’s performance was evaluated in the laboratory and also tested in the field. Vegetation growth and yield for the engineered soil was equal to or better than for the natural top soil, and was also better than combinations of coal waste and ash without the addition of animal wastes, and especially better than the coal waste alone. The initial pH of the engineered soil was greater than 12.0, but decreased to below 8.0 in 3 to 4 weeks. Leachate water showed no toxic levels of the heavy metals As, Cr, Cd, Pb or Hg, although concentrations of SO₄, Ca, Na and Cl were slightly above local groundwater standards.

Harvested vegetation was analysed for plant essential nutrients and heavy metal concentrations. All of the vegetation tested had large concentrations of essential plant nutrients, and Cr, Cd, Pb and Hg were well below toxicity levels. Comparison of pre-growth and post-growth soil showed that the concentrations of Ca, S, B, Fe and Mn were still high. An abundance of these elements was also found in the plant tissue and the leachate water, except for boron, which was not abundant in the water samples.

7.4.2 Environmental Assessment of Ash-Refuse Blends

Daniels et al. (1999) provide data on the interaction of a potentially acid coal refuse (4% total sulphur) with two different alkaline ashes from US power stations. One ash (Clinch River) had a pH of 11 and a calcium carbonate equivalence (CCE) of around 10%; the other (Westvaco paper mill, Virginia) had a pH of 8.5 and a CCE of around 3%. The ashes were blended in varying ratios (0, 5, 10, 20 and 33%) with the coal refuse, and studied using column leaching techniques (24 cm diameter columns filled with 36 kg of refuse). The columns were run unsaturated, and received 25 mm of simulated rainfall per week for a total of 165 weeks. Leachates were analysed for pH, EC, Fe, Mn, SO4 and B
on a regular basis, and for other elements (Ca, Mg, K, Na, Cu, Zn, Al, Ni, As and Se) less frequently.

Pyrite oxidation occurred within the columns, and oxidation effects were clearly visible after testing, especially near the tops of the columns and in the coarser parts of the refuse material. The changes in the columns were further investigated by optical microscopy and SEM investigations. The unamended refuse rapidly produced acidic leachates (pH around 1.7), with high concentrations of dissolved metals (Fe >15,000 mg/l, SO₄ up to 30,000 mg/l and Mn up to 300 mg/l). Columns in which the refuse was blended with the low alkalinity (Westvaco) ash also acidified sequentially over time and also released significant levels of Fe, Mn, Zn and Cu in the eluted leachates. However, refuse blended with high concentrations (20 to 33%) of the more alkaline Clinch River ash produced alkaline leachates (pH >8.4) with low metal concentrations (Al <1.0 mg/l, Cu ~0.10 mg/l, Fe <2.0 mg/l, Mn <3.0 mg/l).

Daniels et al. (1999) suggest that ash addition in this instance has greatly slowed the rate of pyrite oxidation, but did not stop the oxidation process. They suggest that the levels of potential refuse acidity and ash alkalinity should ideally be at least balanced, if not manipulated slightly to the alkaline side. In extreme cases augmentation of the ash with agricultural limestone may also be necessary. Refuse materials with low proportions of total sulphur (<1%) were regarded as better candidates for ash neutralisation by ash materials than the 4% S refuse used in this particular study.

8. PREDICTION OF ASH BEHAVIOUR IN DIFFERENT ENVIRONMENTS

A considerable amount of research has been undertaken in the USA and several other countries, including Australia, with the aim of predicting the extent to which any undesirable contaminants might be liberated from coal ash following interaction with water or other fluids (e.g. Hassett et al., 2005). The ultimate object of this work is to allow any adverse environmental impacts of ash emplacement to be identified by small-scale laboratory tests, as a basis for management and regulation of relevant options for ash disposal or use. Other aspects of leaching tests are discussed by authors such as Theis and Wirth (1977); Dudas (1981); Wang et al. (1999); Georgakopoulos et al. (2002) and Twardowska and Szczepanska (2002).

8.1. Leaching Tests

Leaching tests may be used on coal ash for a number of different purposes, including:

- Acceptance or otherwise of materials as meeting specific regulatory conditions for emplacement or use;
- More extended evaluation of particular materials under particular conditions, as a basis for predicting, managing or monitoring the response to emplacement at a specific project site;
- Scientific research aimed at understanding the factors affecting element mobility, as a basis for improved regulation and prediction frameworks.

Leaching tests involve contacting the material (e.g. ash) with a liquid (e.g. water) to determine which constituents will be released and in what concentrations those
constituents will be leached into the liquid and the relevant environment. A large number of such tests have been developed to help assess the interaction of ashes and other materials with water and other liquids, and the release of any potentially dangerous components to the surrounding groundwater or surface water systems. The various tests address different aspects of leaching, such as the physical mechanisms involved, the chemical interactions between the material and the leaching fluid, the kinetics of leaching and any changes that might be developed as a function of time. As indicated above, different tests may be used for regulatory purposes, environmental impact assessment, scientific research and waste management applications.

A comprehensive summary of some 56 different tests that may be applicable to ash studies was carried out for the American Coal Ash Association by Sorini (1997). The individual tests described in this study vary in terms of test type, leaching aspects addressed and the particular use for which the test was originally designed.

The various tests can be divided into two categories, based on whether or not the leaching fluid is renewed during contact. Tests involving renewal of the leaching fluid are commonly known as dynamic tests, and those in which the leaching fluid is not renewed are commonly referred to as extraction tests. Extraction tests involve a procedure in which the material is contacted with the leaching fluid for a particular interval of time, after which the leaching fluid and test material are separated and the leachate is analysed. In dynamic tests the leaching fluid is intermittently or continuously renewed to maintain the leaching process.

Following from earlier work by Environment Canada (1990), Sorini (1997) divides extraction and dynamic tests each into four sub-categories, as indicated in Table 11. A number of additional methods have also been documented, based on combinations of procedures from different categories.

**Agitated extraction tests** are widely used to characterise the chemical properties resulting from interaction between the test material and the leaching fluid, promoting contact between the test material and the leaching fluid by agitation. A fine particle size for the test material helps to increase surface area and eliminate mass-transfer limitations, reducing the time required to reach steady-state conditions in the fluid and thus the duration of the leaching test.

<table>
<thead>
<tr>
<th>Table 11: Categorisation of leaching tests (Sorini, 1997)</th>
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<tbody>
<tr>
<td><strong>Extraction Tests</strong></td>
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<tr>
<td>• Agitated extraction tests</td>
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<tr>
<td>• Non-agitated extraction tests</td>
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<tr>
<td>• Sequential chemical extraction tests</td>
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<tr>
<td>• Concentration buildup tests</td>
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<tr>
<td><strong>Dynamic Tests</strong></td>
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<td>• Serial batch tests</td>
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<td>• Flow-around tests</td>
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<tr>
<td>• Flow-through tests</td>
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<tr>
<td>• Soxhlet tests</td>
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**Non-agitated extraction tests** are typically used to evaluate any physical mechanisms that limit the rate of leaching, such as the physical integrity of the material. A longer time is required to reach steady-state conditions than with agitated tests, but the role of physical integrity in the leaching process is taken more fully into account.
Sequential chemical extraction tests involve treating the material with a series of different leaching fluids, each being chemically more aggressive than the one used before. The results are often interpreted as reflecting the association of particular leached elements with particular mineral phases.

Concentration buildup tests involve contacting the waste in succession with the same leaching fluid, at low but increasing liquid-to-solid ratios. They are used to model a low volume of water flowing through a large body of waste, nearing saturation with respect to certain contaminants.

Serial batch tests involve repeated contact of the waste material with fresh leaching fluid. The waste and fluid are brought into contact at a specific liquid:solid ratio for a specified time, after which the leachate is separated from the solid phase and fresh fluid is added. The procedure is repeated several times, providing kinetic information on contaminant release and data on release as a function of time. The information is similar to that from column leaching (flow through) tests, but is obtained in a shorter period of time and with a lesser degree of resolution.

Flow-around tests are mostly applied to monolithic materials, and involve contacting a sample of the material in a container with a leaching fluid that is renewed intermittently or continuously. No agitation is normally involved, and the flow of fresh fluid around the sample maintains the leaching process.

Flow-through tests involve passing the leaching fluid through a container packed with the waste material, either in an upward or downward direction, on either a continuous or intermittent basis. One type of flow-through test is the column leaching test, based on a relatively small cylindrical container in either up-flow or down-flow mode. The other is the lysimeter test, conducted in a larger rectangular or cylindrical container usually in down-flow mode. Flow-through tests are generally used for research purposes, and not for regulatory applications or other purposes requiring relatively short test times. Good reproducibility is also difficult to achieve.

Soxhlet tests involve repeatedly boiling, condensing and recirculating the leachate before bringing it into contact with the test material. Although the temperatures are higher than those usually found in nature, analysis of the leachate is often regarded as providing information on the maximum concentrations that can be leached from the test material.

Sorini (1997) provides details of numerous different test procedures in each of these categories, and also of leaching methods involving multiple procedures. Many of the tests have deficiencies, such as covering only a single disposal scenario, specifying test conditions that are unlikely to be met in the field, or providing a leachate not intended to represent that generated in field conditions. Sorini (1997) also indicates that the US-EPA Science Advisory Board has recommended the development of better leaching methods to characterise the leaching and mobility of waste materials, with a need to address the following aspects:

- Developing a better understanding of the mechanisms controlling leaching
- Multiple tests to address different disposal scenarios
- Improved models to complement the leaching tests
- Field validation of leaching tests and predictive models
Sorini (1997) concludes that, despite the numerous tests that have already been documented, relatively long and complex research programs are required to address the items listed above, the results of which can then be condensed into shorter, more simple procedures that can be used as good predictive tools for regulatory purposes and management practices. The long-term objective is therefore to develop simple, rapid and robust test procedures for regulatory and management purposes, based on a sound framework of scientific understanding and backed by relevant validation systems.

### 8.2. Comparison of Test Procedures

One of the principal tests traditionally used for regulatory and management purposes involving ash and other waste materials is the Toxicity Characteristic Leaching Procedure (TCLP), which was originally developed by the United States Environmental Protection Agency in 1984 as a screening test for municipal solid wastes in landfills. This is an agitated extraction procedure (US-EPA Method 1311, US-EPA, 1990a) that, when applied to coal ash, involves shaking the ash for a specified period in a buffered acetic acid solution (pH = 5), followed by analysis of the leachate produced. Experience in TCLP testing of the ashes from Australian coals (e.g. Pathan et al., 2001) indicates that the levels for key elements in most, if not all cases are below the limits typically set on the basis of such data by US regulatory bodies.

The TCLP test is often regarded as representing a worst-case scenario for evaluating the response of ash, especially alkaline ash, to immersion in an acid environment. However, it is increasingly being recognised by the EPA as having limitations for assessing the response of ash in other environmental situations, including those associated with at least some mine backfill and soil applications in Australian conditions. Indeed, as indicated by Sorini (1997), the EPA, in conjunction with other groups, is currently seeking to establish improved test procedures that are more strongly founded in the relevant science and would be applicable to a wider range of environmental assessment tasks.

A similar US-EPA agitated extraction test is the Synthetic Precipitation Leaching Procedure (SPLP), which uses simulated acid rain as the extraction fluid. This procedure (US-EPA Method 1312, US-EPA, 1990b) was originally developed in 1988 for use in evaluating the impact that contaminated soils may have on groundwater. Other methods include the Synthetic Groundwater Leaching Procedure (Hassett, 1987, not listed), which is similar to the TCLP routine except that the leaching solution is made up to represent a synthetic groundwater, rather than the acetic acid solution referred to above. This was developed by the North Dakota Energy and Environmental Research Centre to simulate the response of coal ash in natural groundwater conditions.

An even more simple agitated extraction test is encompassed by ASTM Method D3987, referred to as the Shake Extraction Test (ASTM D 3987, ASTM 1995). This test uses reagent water as the leaching solution, with a liquid:solid ratio of 20:1 and an agitation period of 18 ± 0.25 hours at 18 to 27°C. The method is designed for rapid production of a leachate from solid waste, to estimate the mobility of inorganic constituents. The final pH developed also reflects the interaction of the leaching fluid with the buffering capacity of the waste. The test is not intended to produce a leachate to duplicate that likely to be generated in the field, nor is it intended to be used as the sole basis for engineering design.
A comparison of the results from these tests and a flow-through column leaching test program, based nine fly ashes from power stations in New South Wales, Queensland and Western Australia, was carried out for CCSD by Ward et al. (2004), based mainly on data provided by Killingley et al. (2000). The ashes were divided for the study into two groups, those that yield a neutral to acidic pH on reaction with water and those that yield an alkaline pH.

Four different leaching tests were used by Killingley et al. (2000) in the original study. Three of these were agitated extraction tests, based on agitating a sample of the ash with water or an appropriate solution for a certain time in a sealed container. The fourth was a column leach test, where water was passed through a packed ash column over an extended period of time (12-15 months) and the leachate collected periodically from the bottom of the column in each case. The test procedures were:

- **Shake Test**, based on ASTM Method D-3987, involving water as the leaching solution;

- **Simulated Groundwater Leaching Protocol (SGLP) Test**, based on US EPA Method 1312, in which the leachate was a solution made up to simulate natural ground water;

- **ToxicityCharacteristicLeachingProtocol(TCLP)Test**, following EPA Method 1311, in which the ash was extracted with a buffered acetate solution, selected on the basis of the alkalinity of the ash sample;

- **ColumnLeachingTest**, where around 3 kg of ash was placed in a polycarbonate column 80 mm internal diameter and 980 mm long, and approximately 60 litres (twenty liquid/solid volumes) of de-ionised water passed through the ash in the column over a period of 12-15 months. The cumulative mass of each element extracted at the end of the process was used for comparison to the other techniques.

The effectiveness of the various tests was evaluated using a common index: the relative amount of each element leached from each individual ash sample, expressed as a percentage of that element in the original (unleached) fly ash. This value was calculated for each leaching experiment on each sample, using data provided by Killingley et al. (2000). Because each ash has different concentrations of the various elements, these values provide a better basis for comparison of leaching effectiveness than the absolute proportions of each element released into solution by the different test procedures.

A summary of the results for selected elements is given in Figure 13.

The mobility of elements from the individual fly ashes tested was found to vary significantly, depending on the test procedure used. TCLP testing tends to produce higher levels of leachability for many elements, especially from ashes that generate alkaline leachate solutions, than the other test procedures. This probably reflects the contrast in the pH conditions under which the test is conducted, relative to the pH established by equilibrium with water alone in the other leaching tests. There is evidence that elements such as Ca and Mg, typically abundant in alkali-generating ashes, may occur at least in part in carbonate form, produced by interaction of CaO and MgO with CO₂ in the furnace exhaust gas atmosphere (Bauer and Natusch, 1981). A small peak attributable to calcite (CaCO₃) is also present in the XRD trace of one of the ash samples in the present study.
Such components would probably be more abundant in the alkaline ashes, and also be significantly more soluble under the acid pH conditions of the TCLP test. Although low pH values would also be associated with leaching of the acid-generating ashes by water alone, lesser proportions of carbonate and similar phases would probably be present, resulting in lesser proportions of Ca, Mg and associated elements being released from such ashes even though an acid pH is also involved.

![Graphs of selected elements leached from Australian fly ashes](image)

**Figure 13:** Percentage of selected elements leached from selected Australian fly ashes by different test procedures. Tests (left to right) are: shake, SGLP, TCLP and column. Red and yellow lines represent acid ashes, and blue lines represent alkaline ashes (after Ward et al., 2004).

Elements that followed this pattern, with abnormally high leachabilities under the TCLP procedure relative to the other tests, included As, B, Cd, Co, Cu and Ni, suggesting that at least a proportion of these elements occurs in association with carbonates or similar phases in the fly ashes studied. The TCLP test, however, subjects alkaline ashes to
chemical conditions that are quite different from those derived from immersion in water alone, and similar levels of mobility might not actually be attained from the ashes under more natural exposure conditions.

The column leach test was found to provide similar results for most elements to the simpler shake and SGLP procedures, at least for the samples studied. However, some elements, such as sulphur and, in some acid ashes, copper, appeared not to be released as readily from the column tests, possibly because of re-precipitation in the lower parts of the leaching columns. By contrast, molybdenum and selenium seemed to be more mobile in the column leaching tests, at least from the acid-forming ashes studied, than in the other test procedures. Although the principle of the column leach tests more closely approximates the conditions that might be expected in exposed ash emplacements, the difference in results achieved (with the possible exception of Mo and Se) does not seem from the present study to outweigh their long duration for use as a routine test procedure. They do, however, perhaps provide a better basis for relating the extraction test data to expected field conditions, as exemplified by the difference in S and Mo behaviour.

8.3. Other Evaluations

The Washington State Department of Ecology (2003) have also evaluated a range of different leaching test procedures, as a basis for predicting the impacts of fill material (not necessarily fly ash) on groundwater and surface water quality. Tests evaluated included the TCLP (US-EPA Method 1311) and SPLP (US-EPA Method 1312) outlined above. A literature search conducted by the agency as part of the study revealed relatively little work involving comparisons of laboratory tests to actual field data, and indicated that, of the studies reviewed, the results were mixed in that some leaching tests over-predicted field leaching, some under-predicted, and others provided ambiguous results. For example, the SPLP was found in one study to be more realistic than the TCLP for assessing the mobility of metals in soils. However, the SPLP over-estimated the mobility of most metals (e.g. As, Pb, Zn) but under-estimated the mobility of chromium. These tests (and others) are designed to model a specific leaching scenario (e.g. the TCLP models co-disposal of industrial waste with municipal solid waste) and to measure some intrinsic leaching property (such as solubility in relation to pH), and the results are not expected to match field leachates except where there is a reasonable similarity (e.g. in pH and liquid:solid ratio) between field and laboratory test conditions.

An alternative to the use of single-scenario batch tests is to:

- use a framework to define the question to be answered;
- specify the disposal or use scenario;
- identify the relevant parameters affecting leaching;
- perform tests from a suite of procedures to evaluate those parameters, and
- model the leaching behaviour to simulate and forecast release under the specified time and use scenario.

This step-wise approach is used in Europe to evaluate materials for disposal and beneficial re-use (European Committee for Standardisation, 1997), and a similar framework has been proposed in the USA (Kosson et al., 2002) in response to criticism of the widely-used TCLP. A common theme is the use of a hierarchy of leaching tests in which the type and number of tests is scaled to the type and amount of information required by the user.
A number of studies based on exposing ash to a wider range of test conditions (e.g. Ziemkiewicz et al., 2003; Jankowski et al., 2004; Ziemkiewicz, 2005; Kim, 2005) have shown that the pH of the relevant environment has a particularly strong influence on the mobility of many key elements from individual fly ashes. The results of such studies can also be used in quantitative hydrogeochemical modelling (Jankowski et al., 2005a, b), to understand more clearly the forms into which the elements in the ash are mobilised, and also how the ash and the relevant solution might interact with each other in a natural environmental system. Other factors, such as the oxidation potential, may also be investigated in this way.

8.4. Development of Standard Procedures

Pflueghoeft-Hassett (2002) indicates that the American Society for Testing and Materials is in the process of developing several standards related to the placement of coal combustion products (CCPs) in mines and related settings. These standards, which according to Pflueghoeft-Hassett (2002) are in various stages of the ASTM balloting process, are as follows:

- Guide for the Use of Coal Combustion By-Products for Underground Mine Backfill
- Guide for the Use of Coal Combustion By-Products for Surface Mine Reclamation: Recontouring and Highwall Reclamation
- Guide for the Use of Coal Combustion By-Products for Surface Mine Reclamation: Revegetation and Mitigation of Acid Mine Drainage

The aim of these standards is to provide guidelines for appropriate selection, testing, and placement techniques when CCPs are placed in mine settings. Each standard has a specific scope based on the type of mine placement. The surface mining standards address different types of beneficial uses for CCPs, and will supplement the existing requirements by which the U.S. Department of the Interior Office of Surface Mining (OSM) ensures the environment is protected during coal mining and reclamation. The standards will provide information on appropriate testing and suggest specific tests, as well as provide guidance on how this information can aid individuals/groups associated with the proper placement of CCPs in mine settings.

An summary of the three draft standards is as follows:

**Guide For the Use of Coal Combustion By-Products for Underground Mine Backfill**

This standard guide covers the use of coal combustion by-products (CCPs) for underground mine backfill applications, for the purpose of controlling mine subsidence or for the remediation of acid mine drainage. It does not apply to surface mine reclamation applications. There are many important differences in physical and chemical characteristics that exist among the various types of CCPs available for use in underground mine backfill. Because of physical and chemical characteristics, CCPs commonly used in mine backfill applications are fly ash, flue gas desulfurization (FGD) material, and FBC fly ash. CCPs proposed for each project must be investigated thoroughly to identify the appropriate mix proportions to meet the project objectives. This
The underground mine standard guide incorporates information on formulating the grout for injection; on-site issues such as storage of CCPs, access to water, and site access; and grout injection.

**Guide for the Use of Coal Combustion By-Products for Surface Mine Reclamation: Re-contouring and Highwall Reclamation**

This standard guide covers the use of CCPs for surface mine reclamation applications, as in beneficial use for re-establishing land contours, highwall reclamation, and other reclamation activities requiring fills or soil replacement. The purpose of this standard is to provide guidance on identification of CCPs with appropriate engineering and environmental performance appropriate for surface mine re-contouring and highwall reclamation applications. It does not apply to underground mine reclamation applications. There are many important differences in physical and chemical characteristics among the various types of CCPs available [in the USA] for use in mine reclamation.

CCPs proposed for each project must be investigated thoroughly to design CCP placement activities to meet the project objectives. This guide provides procedures for consideration of engineering, economic, and environmental factors in the development of such applications and should be used in conjunction with professional judgment. This guide is not intended to replace the standard of care by which the adequacy of a given professional service must be judged, nor should this guide be applied without consideration of a project’s unique aspects.

The testing, engineering, and construction practices for using CCBs in mine reclamation are similar to generally accepted practices for using other materials, including cement and soils, in mine reclamation. Physical properties are generally the key to the use of CCPs in re-contouring and highwall reclamation.

**Guide for the Use of Coal Combustion By-Products for Surface Mine Reclamation: Revegetation and Mitigation of Acid Mine Drainage**

This standard guide covers the use of CCPs for surface mine reclamation applications related to area mining, contour mining, and mountaintop removal mining. The issues addressed include: beneficial use for abatement of acid mine drainage, treatment of mine spoils, and revegetation. It does not apply to underground mine reclamation applications.

There are many important differences in physical and chemical characteristics that exist among the various types of CCPs available for use in mine reclamation. CCPs proposed for each project must be investigated thoroughly to design CCP placement activities to meet the project objectives. This guide provides procedures for consideration of
engineering, economic, and environmental factors in the development of such applications.

As in the previous standard guide, the testing, engineering, and construction practices for using CCPs in mine reclamation are similar to generally accepted practices for using other materials. The chemical properties of CCPs are of great importance in identifying appropriate CCPs for revegetation and mitigation of acid mine drainage.

8.5. Possible Approach to Environmental Evaluation

As indicated in other sections of this review, the environmental impacts (if any) when ash is used as mine backfill, are a result of interaction of the ash in a three-component system involving the ash, the mine water or groundwater, and the rock strata in and around the mine site. An environmental testing program might therefore be expected to include studies not only of element mobilities when the ash itself is exposed to water under the conditions (pH, Eh etc) expected at the site, including, for example, any acid mine waters that may be involved, but also the interaction of the products of ash – mine water interaction (i.e. the leachate from the ash) with the associated rock strata. Examples of the latter process include ion exchange reactions with clay minerals, solution of carbonates, and precipitation of salts such as sulphates, carbonates or silicate materials.

As indicated by Jankowski et al. (2004) and, more recently, Dubikova et al. (2006), CCSD research to date has been directed mainly towards investigating the ash-water system, and has reached the point where many of the interactions observed in the laboratory can be explained on the basis of hydrogeochemical modelling techniques. A logical extension of this approach is for the experimental procedures developed for ash-water studies to be extended to investigate the more complex ash-water-rock system in the mine-site context.

It is planned that two different test routines, illustrated in Figure 14, will be investigated as a basis for evaluating such systems, using ash, water and relevant rock samples from selected mine sites.

Figure 14: Possible laboratory test routines to evaluate the interactions of ash, water, and mine rock (or soil) materials.
One of these (Figure 14, left) is a two-step routine, in which the ash and mine water are brought together to produce a leachate, after which that leachate is brought into contact with samples of the mine rock materials. The leachates from both stages of the process will be analysed, and the results evaluated in the light of the solid phase and water characteristics and, to the extent possible, hydrogeochemical modelling techniques. Leaching tests on relevant mine rocks may also be included, to develop a better understanding of the three-component system.

The other routine (Figure 14, right) involves the use of leachability tests directly on appropriate mixtures of the ash and rock materials. This may provide a more rapid basis for testing, but will need to be evaluated in the first instance against results from the two-stage process.

Agitated extraction (shake) tests with relevant leaching solutions will be used in the first instance for these studies, building on the results of CCSD and other research to date. However, flow-through (column-leach) tests may also be included as the program develops, to further evaluate the interactions involved.

9. CONCLUSIONS AND RECOMMENDATIONS

Relatively small quantities of fly ash have been used for mine backfill in South Australia and New South Wales, but such use has declined somewhat since 1998. Coal combustion by-products have also been used for mine backfill in the USA but the quantities used are uncertain. There is a potential in the USA for greatly increased usage of ash for mine backfill, but this potential is hindered by poor public perceptions and lack of reliable scientific data on the environmental effects of such usage. A significant proportion of ash produced in the European Union is used in mining applications, but the actual usage figures are difficult to obtain due to the way such usage is grouped e.g. underground mining with the construction industry.

Regulatory barriers to ash utilisation in Australia under which ash is considered to be an industrial waste tend to inhibit further beneficial usage. Although fly ash is not classified as a hazardous waste in the USA, the requirements of the Surface Mining Control and Reclamation Act must be complied with, and individual states may enact their own legislation. Fly ash is not regarded as a hazardous waste in the European Union, although ash derived from co-combustion is deemed to be hazardous unless proved otherwise.

The environmental effects of the use of ash for mine backfill are uncertain. Although most reviews have indicated an environmentally beneficial or no negative effect, others have suggested that negative effects do occur which may result in contamination of water resources.

The main use of ash in mine backfill has been of alkaline ash in South Africa and the eastern USA, where ash is commonly mixed with the mine solids or mixed with acid waters to ameliorate acid mine drainage conditions. Ash is also emplaced in open-cut mines in the western USA as part of void infill programs, without necessarily an AMD treatment objective. Ash may also be used as a permeability barrier to control water contamination in a number of different settings.
Although backfilling is common in metalliferous underground mines, limited use has been made of ash in underground coal mines. As the ash is used for ground support and subsidence control, the critical factors are the geotechnical properties such as flowability, density, porosity, abrasiveness, strength and pozzolanic or cementitious properties. Most studies on the use of ash in underground mine backfill have focussed on these properties rather than any environmental issues which may arise. Ash has been extensively used in South Africa for underground coal mine backfill with the following properties being considered of importance: proportion of ultra fine particles (<0.01mm) which may impede strength development; maximum practical slurry density, which affects pumping characteristics; ash mineralogy and its effect upon pozzolanic properties of the ash.

Fly ash has also been used for the control of mine fires and as a contaminant barrier to reduce the escape of waterborne contaminants from potentially toxic mine products such as preparation tailings.

Leaching tests have been widely used to assess the likely environmental impacts of ash usage and may be divided into two categories, dynamic in which the leaching fluid is renewed and extraction in which the leaching fluid is in contact with the ash for a specified time interval. These may also be subdivided into four sub categories as shown below.

**Extraction Tests**
- Agitated extraction tests
- Non-agitated extraction tests
- Sequential chemical extraction tests
- Concentration buildup tests

**Dynamic Tests**
- Serial batch tests
- Flow-around tests
- Flow-through tests
- Soxhlet tests

In spite of the number of test procedures currently available, the USA EPA Science Advisory Board has recommended the development of better leaching tests to address the following aspects.

- Developing a better understanding of the mechanisms controlling leaching
- Multiple tests to address different disposal scenarios
- Improved models to complement the leaching tests
- Field validation of leaching tests and predictive models

Comparative studies of the various leaching testes have shown that the mobility of elements from individual fly ashes varies significantly, depending upon the test procedure used. The widely-used TCLP procedure tends to produce higher levels of leachability for many elements, especially from ashes that generate alkaline leachates. Other studies have shown limited correlation of the results of leaching tests with actual field behaviour, and have recommended a stepwise procedure rather than a single scenario batch testing process. The ASTM is currently considering standards for use of coal combustion products in underground mine backfill and surface mine reclamation programs.

This literature review has shown that the potential environmental effects of ash utilisation in mine backfill are not well understood, and that current leaching test protocols may not be an adequate predictor of ash behaviour. Use of ash in mine backfill requires consideration of a three-component system of ash, water (either mine water or
groundwater) and the enclosing rock strata, and any study of the environmental impacts must consider the possible interaction of all three components. Current research within the CCSD has been directed towards an understanding of the ash-water system, and the work program proposed in this report is a logical extension of this research.

It is planned that two different test routines, as illustrated in Figure 14 above, will be investigated as a basis for evaluating ash behaviour in mine backfill systems, using ash, water and relevant rock samples from selected mine sites.

One of these is a two-step routine, in which the ash and mine water are brought together to produce a leachate, after which that leachate is brought into contact with samples of the mine rock materials. The leachates from both stages of the process will be analysed, and the results evaluated in the light of the solid phase and water characteristics and, to the extent possible, hydrogeochemical modeling techniques. Leaching tests on relevant mine rocks may also be included, to develop a better understanding of the three-component system.

The other routine involves the use of leachability tests directly on appropriate mixtures of the ash and rock materials. This may provide a more rapid basis for testing, but will need to be evaluated in the first instance against results from the two-stage process.

Agitated extraction (shake) tests with relevant leaching solutions will be used in the first instance for these studies, building on the results of CCSD and other research to date. However, flow-through (column-leach) tests may also be included as the program develops, to further evaluate the interactions involved.

10. REFERENCES


