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Testing of Interactions between Coal Ash Leachates and Rock Materials for Mine Backfill Evaluations

Colin R. Ward¹,²,*  David French², Leanne Stephenson¹, Ken Riley², Zhongsheng Li¹

¹ School of Biological, Earth and Environmental Sciences, University of New South Wales, Sydney 2052, Australia
² CSIRO Energy Technology, PMB 7 Menai 2234, Australia

A B S T R A C T

A series of laboratory-based leaching tests has been developed to evaluate the chemical interaction between ash, water and different mine-site rock materials, as a basis for assessing the potential environmental impact of using coal ash as backfill in coal mines. Two different test protocols were used: a two-stage serial batch testing program in which leachate from representative ash samples were allowed to interact separately with relevant rock materials under laboratory conditions, and a single-stage mixed batch testing program in which 50:50 mixtures of the same ashes and rock samples were extracted with water following a similar procedure to leaching tests used for the individual ash and rock samples.

The concentrations of major and trace elements released in both studies were compared to the concentrations expected in the relevant experiments from the leaching characteristics of the individual ash and rock samples when tested alone. In both the serial tests and the mixed-batch tests these showed markedly lower concentrations of several key elements in solution (e.g. Mo, As, Se) after interaction of the ash leachate with the rock samples. The results indicate that some elements released from the ash in a mine backfill may be attenuated to a significant extent when the leachate comes into contact with other rock materials. The extent of attenuation was greatest for rocks with high proportions of clay minerals (e.g. shales) or Fe oxy-hydroxides (e.g. iron-stained sandstones). Rocks with lower clay or Fe oxy-hydroxide contents, such as white quartz sandstones, apparently have lesser attenuating effects.

The attenuation properties appear to be related to the nature of the rock in question, and test programs of this type may provide a useful basis for assessing the potential impacts of placing different ashes in close association with relevant rock strata in mine backfill and similar applications. Although testing for any individual site should also consider the design of the proposed backfill, the regional hydrogeology and the results of other site investigations, collection and evaluation of data from one or both procedures may be of value in more fully understanding and predicting the environmental impact of ash-based mine backfill programs.

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A R T I C L E  I N F O

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1. Introduction

The use of coal ash in backfill and remediation of mine excavations is gaining increased attention from the power and mining industries as a more beneficial process of ash disposal (Vories, 2001; National Research Council, 2006; Ward et al., 2006; 2007a). Specific applications of ash in the mining industry 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;

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- 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; and
- Improvement of natural or artificial soils in mine-site rehabilitation programs.

The most commonly reported benefits of ash in mine backfill are typically those arising from the interaction of alkaline ash with mine solids, mine waters, or in mining voids to ameliorate acid mine drainage (AMD) conditions (e.g. Branam et al., 1999; Murarka, 2001; Reynolds, 2005; Akcil and Koldas, 2006; Dutta et al., 2009). However, ash is also routinely emplaced in a range of other mine settings as part of backfilling programs, e.g. in open-cut coal mines in the western USA (Koehler, 2002; Young, 2002), without necessarily an AMD involvement; this suggests a potential for similar use in wider mine-site applications.

Ash-based backfill may be used for ground support and subsidence control in underground mines (Ilgnier, 2000; ACARP, 2001; Potvin et al., 2005), an application in which the critical factors are flowability, density, porosity, abrasiveness, strength, and pozzolanic properties. Fly ash has been used for the control of mine fires (McNally, 1997; Colaizzi, 2004), as a contaminant barrier to reduce the escape of waterborne contaminants from potentially toxic mine products such as preparation tailings (Nhan et al., 1996; Shang and Wang, 2005), and as an additive to enhance the fertility of mine soils in reclamation programs (Stewart et al., 2001; Mittra et al., 2005).

Coal ash, however, is generally considered to be an industrial waste, and as such is subjected to greater regulatory controls than equivalent virgin (e.g. directly mined) materials with equivalent potential impacts (Nairn et al., 2001; Vories, 2001; Aynsley et al., 2003; Riley, 2005; Heeley, 2007). This often has the effect of making virgin materials more attractive than ash for particular purposes, even though the ash may be equally or not more suitable from the technical point of view.

Gaining approval to emplace fly ash into an existing mine would generally require the same range of technical information as for any other proposal with potential for adverse environmental impacts. As indicated by the National Research Council (2006), this would include:

- The chemistry and mineralogy of the material;
- Likely contamination from the ash and how it would be contained;
- Dust suppression, noise, truck movements etc;
- Impact on ground water;
- Impact on the community.

Emplacement of fly ash into an operating or worked-out mine, rather than establishing a separate ash emplacement area in otherwise undisturbed or productive terrain, has a number of environmental advantages, and these may further encourage acceptance by regulatory authorities and communities of emplacement proposals meeting the necessary technical requirements. Although technical studies of ash placement in mines (e.g. Vories, 2001) typically show that the ash is neutral if not beneficial in its environmental impact, ash emplacement may inherently add some environmental risk to the mine’s operation (Norris, 2004). Mine operators might therefore require additional benefits from the ash emplacement, such as payment for accepting the ash, availability of material for particular purposes at less cost than alternatives, or operational benefits such as truck back-loading.

2. Environmental Evaluation of Ash for Backfill Applications

In addition to geotechnical properties, which are a significant factor in applications such as support of underground openings (Ilgnier, 2000; Potvin et al., 2005), one of the main issues that may be associated with ash emplacement is the possibility that undesirable concentrations of environmentally significant elements may be leached from the ash into the surrounding groundwater or surface water systems (Singh and Paul, 2001). A considerable amount of research has been carried out on the interaction of coal ash with water, with special focus on the mobility of environmentally significant trace elements in both short and long-term leaching processes (e.g. Theis and Wirth, 1977; Dudas, 1981; Grisafe et al., 1988; Eary et al., 1990; Jones, 1995; Sorini, 1997; Querol et al., 2001; Ziemkiewicz et al., 2003; Hassett et al., 2005; Ness et al., 2007). As well as the modes of element occurrence within the ash, this has shown that the pH of the ash-water system exerts a major control on the mobility of different elements (e.g. Kim et al., 2003; Jankowski et al., 2006; Dubikova et al., 2006), including those of potential environmental significance. Ash pH in turn depends on ash chemistry, particularly the balance between the concentration of alkaline-earth elements, Ca and Mg on the one hand and the proportion of potentially acid-generating sulphates and phosphates on the other (e.g. Querol et al., 2000; Killingley et al., 2000). The leachates from fly ashes may range from fairly acid (around pH = 4) to relatively alkaline (pH = 12), depending on the ash chemistry (Killingley et al., 2000; Bear et al., 2003; Jankowski et al., 2006; Ward et al., 2009), and the ash chemistry is in turn controlled by the mineral matter in the feed coal (Ward and French, 2006; French et al., 2007).

Most of the research on ash leaching has been directed towards study of two-component ash-water systems. The interactions when ash is used as mine backfill, however, occur within three-component systems involving the ash, the mine water or ground-water, and the rock strata in and around the mine site. Test programs to establish the environmental behaviour of a particular ash in a given mine backfill application should therefore include studies not only of element mobility when the ash itself is exposed to water under the conditions (pH, Eh etc.) expected at the site, but also of the behaviour of the products of ash – mine water interaction (i.e. the leachate from the ash) when brought into contact with the associated rock strata.

A logical extension of the two-component approach is therefore to investigate the more complex ash-water-rock system in a mine-site context. Although a significant amount of work has been carried out on the interaction of alkaline ash leachates with mine rocks in situations associated with acid mine drainage (e.g. Daniels et al., 1999; Reynolds, 2005; Sureneder and Petrick, 2005), only limited information is available on assessment methods and protocols for assessing the interactions between ash, rock and water in other situations (e.g. acid ashes and/or mines without AMD), as a basis for better managing the environmental risks, if any, associated with mine backfill operations. The present paper represents an attempt to address this deficiency by describing two different test protocols to evaluate the elements released from particular ashes, and more particularly the interaction of those elements with the mine rock.
elements with the different rock strata with which the ash leachate may come into contact at the emplacement site.

To develop a framework for evaluating more fully the possible processes in the ash-rock-water system, a series of studies has been undertaken to investigate the interactions between the fly ash from a number of different Australian power stations and a range of rock types from nearby open-cut coal mines. Most of the fly ash at these power stations is currently emplaced in ash ponds (Ness and Heele, 2007). However, the ponds are approaching the limits of their storage capacity, and other sites, including worked-out areas of adjacent coal mines, are therefore under consideration for future ash emplacement. New mining and power station projects in these and other areas are also considering ash placement in mines as an option for future ash management programs.

Ash for backfill of open-cut mines is typically emplaced as discrete lenses or layers, surrounded by or perhaps more intimately mixed with excavated and emplaced overburden materials (Vories, 2001; Luther et al., 2005; Ward et al., 2007a). Any leachate derived from water passing through the ash would thus be expected to permeate through the surrounding fragmented overburden, providing opportunities for the ash leachate to interact with the different mine rock materials. The changes developed when ash leachate comes into contact with mine rock materials are therefore of great significance in determining the impact of ash emplacement in the context of the backfill operation, and thus represent the main focus of the present paper.

### 3. Samples and Sample Characteristics

#### 3.1 Sample collection

Fresh fly ash samples were obtained from pulverised fuel power stations in the Tarong Basin of Queensland, containing bituminous coal of Triassic age (Pegrem, 1995), and the Collie Basin of Western Australia, containing subbituminous coal of Permian age (Ashton et al., 1995). Bottom ashes and in some cases long-stored fly ashes were also collected, but these are not discussed in the present paper. In addition to the ashes, a range of representative rock samples was taken from exposures in open-cut coal mines associated with the power stations, to represent the range of material with which leachates from the ash would be likely to come into contact in a mine backfill operation.

#### 3.2 Sample characterisation

The rock samples were air-dried and crushed to <5 mm, with representative splits being further ground to <63 μm for chemical and mineralogical analysis. The ashes were air-dried where necessary, and representative splits also finely ground for chemical analysis.

### Table 1

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Abbrev’n</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>MnO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>LOI</th>
<th>pH</th>
<th>EC</th>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>Ash</td>
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<td>31.2</td>
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<td>1.65</td>
<td>0.11</td>
<td>0.20</td>
<td>0.032</td>
<td>&lt;0.01</td>
<td>0.33</td>
<td>0.059</td>
<td>0.01</td>
<td>&lt;0.5</td>
<td>6.97</td>
<td>488</td>
</tr>
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<td>22.5</td>
<td>1.04</td>
<td>3.54</td>
<td>0.24</td>
<td>0.80</td>
<td>0.035</td>
<td>0.20</td>
<td>1.88</td>
<td>0.061</td>
<td>0.09</td>
<td>11.6</td>
<td>6.49</td>
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<td>0.02</td>
<td>0.09</td>
<td>0.026</td>
<td>0.31</td>
<td>0.15</td>
<td>0.027</td>
<td>&lt;0.01</td>
<td>0.48</td>
<td>0.032</td>
<td>0.23</td>
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<td>Tailings</td>
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<td>17.5</td>
<td>0.67</td>
<td>0.73</td>
<td>0.06</td>
<td>0.15</td>
<td>0.018</td>
<td>&lt;0.01</td>
<td>0.48</td>
<td>0.032</td>
<td>0.23</td>
<td>45.1</td>
<td>6.22</td>
<td>205</td>
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<tr>
<td><strong>Collie Basin Samples</strong></td>
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<td></td>
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</tr>
<tr>
<td>Collie Power Station fly ash</td>
<td>Collie</td>
<td>45.7</td>
<td>25.9</td>
<td>1.41</td>
<td>17.7</td>
<td>2.39</td>
<td>1.50</td>
<td>0.13</td>
<td>0.35</td>
<td>0.49</td>
<td>1.55</td>
<td>0.56</td>
<td>1.20</td>
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<td>Lt gy sh</td>
<td>46.1</td>
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<td>0.50</td>
<td>0.04</td>
<td>0.12</td>
<td>0.01</td>
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<td>0.51</td>
<td>0.12</td>
<td>0.19</td>
<td>29.3</td>
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<td>80</td>
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<tr>
<td>Ewington Mine hard sandstone</td>
<td>Hd ss</td>
<td>67.3</td>
<td>19.1</td>
<td>0.99</td>
<td>0.35</td>
<td>0.02</td>
<td>0.07</td>
<td>0.01</td>
<td>0.02</td>
<td>0.22</td>
<td>0.05</td>
<td>0.12</td>
<td>11.8</td>
<td>3.54</td>
<td>554</td>
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<tr>
<td>Ewington Mine white sandstone</td>
<td>Wh ss</td>
<td>91.6</td>
<td>5.9</td>
<td>0.47</td>
<td>0.18</td>
<td>0.01</td>
<td>0.06</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>2.5</td>
<td>5.60</td>
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<tr>
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<td>Carb sh</td>
<td>18.7</td>
<td>12.2</td>
<td>0.58</td>
<td>0.22</td>
<td>0.03</td>
<td>0.06</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.15</td>
<td>0.02</td>
<td>0.34</td>
<td>66.9</td>
<td>4.38</td>
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<td>45.4</td>
<td>27.9</td>
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<td>13.1</td>
<td>1.45</td>
<td>1.20</td>
<td>0.05</td>
<td>0.48</td>
<td>0.47</td>
<td>1.00</td>
<td>0.38</td>
<td>7.1</td>
<td>5.50</td>
<td>1665</td>
</tr>
<tr>
<td>Premier Mine white sandstone</td>
<td>Wh ss</td>
<td>85.5</td>
<td>10.1</td>
<td>0.48</td>
<td>0.41</td>
<td>0.02</td>
<td>0.06</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.11</td>
<td>0.02</td>
<td>0.12</td>
<td>3.8</td>
<td>6.04</td>
<td>37</td>
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<tr>
<td>Premier Mine grey shale</td>
<td>Gy sh</td>
<td>39.6</td>
<td>17.3</td>
<td>0.83</td>
<td>0.58</td>
<td>0.04</td>
<td>0.16</td>
<td>0.01</td>
<td>0.09</td>
<td>0.80</td>
<td>0.04</td>
<td>0.27</td>
<td>38.9</td>
<td>4.40</td>
<td>342</td>
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</table>

**Notes:** pH and EC taken from 3-day single batch tests.

### Table 2

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Trace element chemistry of ash and rock samples (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tarong Basin Samples</strong></td>
<td></td>
</tr>
<tr>
<td>Tarong North PS dense phase ash</td>
<td>22 5.2 25 65 226 66 212 44 27 70 124 8 0.99 3.2 110</td>
</tr>
<tr>
<td>Meanda coal mine sandstone, white</td>
<td>1 0.3 7 120 12 99 195 5 19 6 9 3 &lt;0.05 1.1 30</td>
</tr>
<tr>
<td>Meanda coal mine silstone/shale</td>
<td>24 3.5 18 470 117 64 286 24 22 32 95 10 0.18 1.2 25</td>
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<td>Meanda coal washerily tailings</td>
<td>12 1.5 20 350 72 12 70 8 &lt;1 18 97 5 0.17 2.4 32</td>
</tr>
<tr>
<td><strong>Collie Basin Samples</strong></td>
<td></td>
</tr>
<tr>
<td>Collie Power Station fly ash</td>
<td>26 26 40 59 61 8 960 8 5 110 450 31 4.45 39 7</td>
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<td>Ewington Mine light grey shale</td>
<td>7 2 9 210 96 66 20 9 24 40 73 8.1 0.82 2.2 0.4</td>
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<tr>
<td>Ewington Mine hard sandstone</td>
<td>&lt;2 &lt;0.3 10 140 51 27 20 5 36 10 20 7.4 0.37 2.0 &lt;0.1</td>
</tr>
<tr>
<td>Ewington Mine white sandstone</td>
<td>2 &lt;0.3 5 67 34 &lt;1 10 3 3 &lt;6 &lt;5 7.9 &lt;0.05 1.6 &lt;0.1</td>
</tr>
<tr>
<td>Ewington Mine carbonaceous shale</td>
<td>&lt;2 3.3 9 98 34 37 10 12 24 10 40 2.0 1.06 2.8 2.3</td>
</tr>
<tr>
<td>Muja Power Station Units C-D fly ash</td>
<td>21 24 33 140 34 29 360 5 17 99 340 30 9.28 32 11</td>
</tr>
<tr>
<td>Premier Mine white sandstone</td>
<td>2 &lt;0.3 8 72 12 11 8 1 28 &lt;6 &lt;5 1.4 0.13 0.6 &lt;0.1</td>
</tr>
<tr>
<td>Premier Mine grey shale</td>
<td>24 4.7 10 160 58 63 38 16 62 30 93 3.2 0.91 1.8 1.4</td>
</tr>
</tbody>
</table>
and mineralogical studies. Fused borosilicate disks were prepared from the ash and rock samples, and analysis of the major elements was carried out using X-ray fluorescence (XRF) spectrometry techniques. The loss on ignition at 1050 °C was also determined as part of the sample preparation process.

Trace element concentrations in the ash and rock samples were determined mainly by ICP-AES or ICP-MS techniques, following either dissolution of the samples in mixed mineral acids or lithium borate fusion and subsequent acid dissolution. Boron was determined by ICP-AES after fusion in Eschka mixture and selenium by hydride generation AFS following HF digestion of the samples.

Mineralogical analysis of the ash and rock samples was carried out by X-ray powder diffraction, with quantification of the phases present using the Rietveld-based Siroquant software system (Taylor, 1991; Ward et al., 1999; Ward and French, 2006). Poorly-crystallised tridymite (Tarong Basin) and metakaolin phases (Collie Basin) were incorporated into the analysis tasks, as described by Ward and French (2006), to provide an estimate of the proportion of amorphous material in each of the ash samples.

### 3.3 Composition of ash and rock samples

Detailed characteristics of the ash and rock samples taken for the study are given in open-file reports by Ward et al. (2007b; 2008), accessible through the Pandora database of the National Library of Australia (http://pandora.nla.gov.au). Fresh fly ashes from each basin, together with a subset of rock samples representing different types of shale, sandstone and in one case coal preparation refuse (tailings) from the associated open-cut mines (Table 1), were used for the more detailed studies outlined in the present paper. Major element data for these samples are given in Table 1, and concentrations of selected trace elements in Table 2. Quantitative data on the minerals identified from the XRD studies, including, for the ashes, the proportion of amorphous (or glassy) material, are given in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quartz</th>
<th>Mullite</th>
<th>Cristobalite</th>
<th>Gehlenite</th>
<th>Hematite</th>
<th>Maghemite</th>
<th>Hercynite</th>
<th>Spinel</th>
<th>Pyroxene</th>
<th>Rutile</th>
<th>Halite</th>
<th>Amorphous</th>
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<td>69.3</td>
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<td>1.4</td>
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<th>Chlorite</th>
<th>Siderite</th>
<th>Microcline</th>
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**Fig. 1.** Flow-sheet illustrating two-stage serial batch tests (left) and 50:50 mixed batch tests (right) used in the mine backfill study.
The leaching characteristics of each ash and rock sample were tested by extracting the materials with deionised water in a series of individual batch tests, based on procedures described by Jankowski et al. (2006). Although solutions with strongly buffered pH values may be of use in evaluating some of the fundamental processes affecting mobility, authors such as Hassett et al. (2005) indicate that testing for field emplacement should be carried out under conditions that mimic as closely as possible those likely to be encountered in the relevant natural setting. Use of deionised water allowed the ash-water and rock-water interactions to take place at the natural pH levels associated with the materials in question. Ideally such testing should use groundwater from the mine site, to allow for the impact of its pH, or of any elements already in solution (Ziemkiewicz et al., 2003; Hassett et al., 2005); however, this was impractical for the present study, due to the distant location of the test site with respect to the laboratory and the possibility of changes to water chemistry during transportation and storage.

Samples of 32 grams of air-dried ash or air-dried and crushed (<5 mm) rock sample were weighed into polyurethane bottles and 112 grams of deionised water added, making the liquid:solid ratio 3:5:1. Although larger-sized rock particles and larger volumes of water would be expected in an actual mine backfill, testing at such sizes is clearly not possible in the laboratory situation. The use of finer rock particles (<5 mm), combined with the relatively low liquid:solid ratio of 3:5:1, was intended to allow similar interactions to occur in the smaller water volumes of laboratory batch tests.

The bottles were sealed and shaken on a horizontal shaker at 110 rpm at room temperature for periods of 1, 3 and 7 days, after which the solutions in each bottle were separated out by drawing through 0.22-μm cellulose acetate membrane filters. Approximately 30 ml of each extract was immediately acidified using 10 drops of concentrated nitric acid prior to major and trace element determinations using ICP-AES and ICP-MS techniques. The remaining non-acidified leachates were subjected immediately after sample collection to measurement of pH and electrical conductivity (EC), and to HCO₃⁻ determination by titration.

5. Evaluation of Ash-Rock-Water Interactions

Two different batch tests involving combinations of ash and rock samples, referred to as serial batch tests and mixed batch tests, were used to assess the possible interactions associated with the ash-rock-water system in mine backfill situations (Figure 1).

5.1 Serial batch tests

The serial batch tests were based on leaching of each ash sample followed by use of the leachate from that ash to test the interaction of that ash leachate with typical rock materials at the relevant mine site. These tests were intended to evaluate the impact of a scenario in which water passes through a deposit of ash and continues into different types of fragmented or in-situ rock materials. In such a scenario, the water would first reach equilibrium with the ash, after which a second equilibrium
would be developed between the ash leachate and the surrounding rock strata.

Six samples of 32 grams of each ash were weighed into polyurethane bottles and 112 grams of deionised water added, as for the individual batch tests on the same materials. The bottles were sealed and shaken for 3 days, after which the leachates for each ash were filtered through 0.22-μm cellulose acetate membrane filters and pooled. A portion of the pooled leachate for each ash was set aside and analysed as a check against the individual batch test results for the same ash sample.

In the next part of the test 32 gram samples of each rock were weighed into polyurethane bottles and 112 grams of the relevant ash leachate added, keeping the liquid:solid ratio 3.5:1 as for the individual batch tests described above. The bottles were sealed and shaken for 7 days, after which the solutions in each bottle were filtered, aliquots acidified for analysis of their major and trace components, and other aliquots subjected to pH and EC determination.

5.2 Mixed batch tests

The mixed batch tests involved leaching experiments on mixtures made up of each ash and each of the relevant rock samples. These were intended to represent a situation in which ash and rock were in contact with the water simultaneously, such as might occur if a more intimate blend of ash and mine rock is used as the backfill material. The equilibrium developed in this case would not necessarily be the same as with the serial tests, since the ash remains in contact with the water and a three-way equilibrium involving ash, rock and water is developed.

Samples of 32 grams containing 50:50 mixtures of each ash and each of the relevant rock samples were weighed into polyurethane bottles for the mixed-batch tests, and 112 grams of deionised water added to provide a liquid:solid ratio of 3.5:1. The bottles were sealed and shaken for 7 days. The solutions in each bottle were then filtered, aliquots acidified, and the acidified and untreated samples analysed as for the serial batch tests.

6. Results and Discussion

The pH and electrical conductivity of the leachates from the individual ash and rock samples are listed in Table 1. Plots showing the pH, electrical conductivity, and selected major and trace elements in each sample for the serial tests and the mixed batch tests are presented in Figures 2 to 7. The complete results obtained from the program, including similar plots for a wider range of elements and the full data set for the individual batch tests, serial batch tests and mixed batch tests, are given in open-file reports by Ward et al., 2007b; 2008), accessible electronically through the National Library of Australia.

Figures 2 to 7 show the concentrations obtained for each test in comparison to the values expected from the mixture of materials used in each case. The expected values were derived from the individual batch test results following procedures described in more detail below. It should be noted that the concentration values on the vertical axis of each plot are different, reflecting the
absolute values of concentration in solution for each of the elements and samples involved.

6.1. Serial batch leaching tests

To provide a basis for evaluating the results from the serial batch tests, the concentration of each element (and also the pH and electrical conductivity) expected after the two stages of each serial batch test was estimated based on the sum of the concentrations of that element released from the ash after three days and the rock in question after seven days in the respective individual batch tests. Such an expectation is based on the assumption that the elements released from each material in the two-stage test would be additive, i.e. if a concentration of \(x\) units was released from the ash after the first stage of the experiment and a concentration of \(y\) units was added to the leachate from the rock sample in the second stage, the expected element concentration from the two-stage process would be \(x+y\) units.

The results obtained from the serial batch tests for selected components in relation to these expectations, as well as for the same components released from each individual ash itself in two separate single-batch experiments, are summarised in Figures 2 to 4.

The validity of the assumptions in relation to the overall expectations appears to be borne out by the results obtained from the electrical conductivity data for the individual (Table 1) and serial batch tests (Figure 2). Although each ash sample when tested alone had a relatively high conductivity in relation to the rocks in the relevant test series, the conductivity of the leachates from most of the serial tests was higher still, with the increase in each case being very close to the conductivity of the relevant rock sample when tested in the individual batch studies.

Although there is some variation, the pH values of the leachates after the tests were in most cases close to the levels expected from individual batch tests of the respective ash and rock samples (Figure 2). This suggests that the rocks tested have a significant buffering capacity, probably derived from their abundant clay minerals. In a few cases, however, especially with the sandstones, the pH remained similar to that of the relevant ash leachate found in the single batch tests. This probably indicates that the rock in question has a relatively low buffering capacity, possibly because of a lower clay mineral content.

The concentration of the various elements in solution when ash leachates are exposed to different rock types, as in the serial batch tests, may be expected to fall into one of three categories:

a) The element concentration in the leachate increases to a level approximating that expected from the combination of the two individual leachate solutions, suggesting that the rock in question continues to release a particular concentration of that element regardless of the other components (in this case derived from the ash) also present in the surrounding solution;

b) The element concentration increases above the expected level, suggesting that the rock releases a greater concentration of that element when the ash leachate is introduced than it would with water alone;
c) The element concentration is less than that expected from the combined leachates, suggesting that the presence of the rock material causes no more, and indeed possibly less of the element to be released from the rock when the ash leachate is present. Two possibilities arise in such circumstances:

i. The concentration associated with the rock remains essentially the same as with the ash alone, suggesting either that the element is at saturation with respect to the rock, or that the rock has no impact on the element concentration released by the ash sample. This is equivalent to category (a) above, in cases where the rock when tested alone releases no significant concentration of the element in question.

ii. The element concentration after interacting with the rock falls significantly below that in the original ash leachate, suggesting that the element in question may have either been precipitated in some form, or it may have been taken up by sorption, ion exchange, or some other process into the rock components.

Calcium and Al for the Collie Basin samples and S (expressed as SO$_4^{2-}$) for all of the ashes are the only elements among those plotted in Figures 2–4 where the concentrations in the second leachate were consistently close to those expected by addition of the individual leachate solutions (category (a) above). A number of other elements that were not plotted, such as Si, Na, and B, also show similar behaviour (see Ward et al., 2007b, 2008).

Magnesium shows a higher concentration than expected in the leachates (category (b) above) for all of the Tarong rock samples and for the shale samples from the Collie Basin (Figure 3), suggesting that additional release was stimulated by introduction of the ash leachate solution. The Mg concentrations from the Collie Basin sandstones tested with Collie Basin ashes, however, were close to the levels expected from the solution mixing calculations.

Most of the remaining elements, including Ca and Al from the Tarong samples and Mo, Se, and As from the entire sample series, although often relatively mobile from the ash alone, have much lower concentrations after the ash leachate has interacted with at least some of the rock samples (category (c)ii). The sandstone samples in some of these cases (e.g. Mo for Tarong) do not seem to have had a great impact (category (c)i), but the concentrations in solution are significantly lower after exposure to the shale and the coal tailings materials from Tarong as well as most of the rocks in the Collie Basin study.

6.2. Mixed batch leaching tests

The concentration of each element (and also the pH and electrical conductivity) expected after leaching of the ash-rock mixture in the mixed batch tests was estimated based on half the sum of the concentrations of that element released from the ash after three days and the rock in question after seven days in the individual batch tests. Such an expectation is based on the fact that only half the mass of ash and half the mass of rock was in contact with the volume of leaching solution used, compared to each of the
relevant single-batch tests. Hence, the elements released from each material in the mixed-batch test, if additive, would be the sum of those two half-concentrations: i.e. if a concentration of x units was released into the test volume from the ash in the relevant single sample test and a concentration of y units was released into that volume from the rock sample in the relevant single sample test, the expected element concentration from the mixed batch process would be \((x + y)/2\) units.

The results for the mixed-batch leaching tests (Figures 5–7) are similar overall to those of the serial leaching tests, especially for the Tarong sample series, but with lesser contrast developed between ash and ash plus rock than with the two-stage serial test program. The leachate pH values for the ash-rock mixtures (Figure 5) are relatively close to expectations, but most tend to be closer to the pH of the leachate from the ash with water alone (Table 1) than to the pH of the respective rock materials. This suggests that the buffering capacity of the ash is stronger than that of the rock samples, and hence that the pH of an ash-rock mixture, at least for the samples studied, would probably depend more on the ash characteristics than on the rock type involved.

The electrical conductivities of the mixed batch leachates were close to but generally slightly higher than the values expected based on the individual leaching tests. As with the serial batch tests, this suggests that elements released from both components contribute to the overall leachate derived from the test procedure. Specific individual elements, however, behave somewhat differently, as indicated in the discussion below.

As with the serial batch tests, the concentrations of S (as \(\text{SO}_4\)) for all samples and Ca for the Collie Basin materials was close to expectations in the mixed batch tests (Figures 5 and 6. In contrast to the serial test results, however, the concentrations of Al in solution with the tests involving the ash from both the Tarong and Collie Power Stations were considerably below expectations.

In addition to Al as discussed above, the concentration of Mo was also lower than expectations for the tests in the mixed batch series involving shales and coal tailings (Figure 7), but close to or above expectations when the ashes from both stations were mixed with the respective sandstone samples. The concentrations of Se and As were also lower than expected for the Tarong ash-rock mixtures, but close to or above expectations for the Collie Basin samples.

For those elements where the concentration in the mixed batch tests was lower than expected it appears, as with the serial tests, that some of the element in question has been taken up by the rock components. Especially with Tarong, but also with Mo in the Collie Basin tests, the effect is more marked in the mixtures involving the shale and tailings samples, and sandstones appear to have had less of an impact on the element concentration in the mixed-batch leachate solutions.

The results of the two test programs suggest that the coal mine rock materials, particularly the overburden shales, clay-rich coal preparation refuse, and ferruginous sandstones, appear to interact with leachates from emplaced ash and reduce the concentration of some of the environmentally significant trace elements that might otherwise be released from the ashes if used as part of a mine
backfilling or similar program. If so, it may follow that the concentration of some potentially significant trace elements released into percolating waters from a mine-site ash deposit may be at least partly attenuated by contact of the ash leachate with the adjacent rock strata. The attenuation behaviour appears to be related to the nature of the rock in question, and may thus provide a basis for more fully assessing the potential impacts of different ashes in relation to relevant rock strata for mine backfill projects.

### 6.3. Processes affecting element attenuation

As discussed more fully by Ward et al. (2007b), processes responsible for the reduction in dissolved concentration or (partial) element immobilization when ash leachate interacts with rock materials may include:

- Precipitation, due to factors such as pH change or interaction with other ions, released into solution from the rock material;
- Adsorption, representing attachment of ions from solution on to the surface of relevant mineral particles, such as Fe oxy-hydroxides or clay minerals;
- Ion exchange, where ions in solution replace other ions held on or within the crystal structure of particular minerals, again such as Fe oxy-hydroxides or clay minerals.

The pH of the leachate solutions from individual batch testing of the ashes and rocks for the present study are very similar (Table 1), especially for the samples from the Tarong Basin. Similar pH values are also noted for the serial and mixed batch tests (Figures 2 and 5), and thus precipitation processes associated with major pH change are unlikely to be involved in the reductions in element concentration observed in the present study when the ash leachates interact with the rock materials.

Several studies of element mobility from coal ash (e.g. Eary et al., 1990; Querol et al., 2001; Kim et al., 2003), including hydrogeochemical modelling of the behaviour of elements leached from Australian ashes (Jankowski et al., 2005; Dubikova et al., 2006), indicate that Mo, Se, and As, the concentration of which is most affected by the interaction of ash leachates with rock materials in the present study, behave as oxy-anions (e.g. MoO$_4^{2-}$) in laboratory leaching tests. Similar behaviour also appears to occur under field conditions (Ward et al., 2007c; 2009). The possibility of precipitation as a process for element immobilization was therefore further investigated for the Collie Basin samples by Ward et al. (2007b) using hydrogeochemical modelling techniques (cf. Wang et al., 1994).

Saturation indices for most of the elements from the Collie Basin evaluated using the PHREEQC modelling system (Parkhurst and Appelo, 1999), including the different forms of Mo (Figure 8), were found to remain below zero under the experimental conditions of the serial and mixed batch tests. The modelling did, however, suggest that CuMoO$_4$ and CdMoO$_4$ may have saturation indices above zero (i.e. be insoluble species) in the natural pH range associated with the combined ash and rock samples in the mixed batch tests (Figures 8C and 8D). Although probably only a minor factor, precipitation might therefore possibly explain some of the attenuation of Mo observed on contact with the rocks in the test.
program. Precipitation as CuMoO$_4$ might thus possibly contribute to the immobilisation of Cu, noted along with Mo for some of the rock samples in the serial and mixed batch tests (Ward et al. 2007b).

The behaviour of the key trace elements in the present study is also consistent with pH-controlled adsorption of the different elements on to Fe-oxides and clay minerals (cf. Thornber, 1985). The extent of any such adsorption would depend on the element concentration in solution and the solution pH, and, to a lesser extent, on factors such as the adsorbing particle concentration, solution ionic strength, temperature, and the concentration of any competing ions that may be present.

Under neutral to slightly acidic conditions, such as those observed for the Tarong and Collie Basin samples, trace elements that form oxy-anions in solution tend to be adsorbed on to goethite and/or clay minerals due to the weak positive charge that develops on the mineral surfaces (Farley et al., 1985). Trace elements which are stable as simple cations (such as Co, Ni, Zn) tend not to be adsorbed in such circumstances, but may be adsorbed under more alkaline pH conditions.

Because the greatest attenuation effects in the present study are associated with rocks rich in clay minerals or poorly crystalline Fe oxy-hydroxides, adsorption by the clay minerals or Fe oxy-hydroxides in the rocks may be the principal mechanism responsible for the reduction in trace element concentration when the ash leachate comes into contact with the rock materials. Research on other materials (e.g. Wangen and Williams, 1982; Jenne, 1998; Goldberg and Forster, 1998) indicates that species showing anionic characteristics, such as Mo, Se, and As, are relatively strongly adsorbed on to Fe oxy-hydroxides (e.g. goethite), and also on to clay minerals, under mildly acid pH conditions (pH 4 to 6) similar to those encountered with the ashes in the present study.

The decrease in concentration of some ions, such as Ca in the Tarong series, and the associated increase in Mg for the same series, is also consistent with ion exchange processes in the rock-water system. Such processes would represent an extension of the adsorption/desorption reactions discussed above, and thus further confirm that type of reaction as the principal mechanism responsible for the attenuations of the elements observed in the leachate solutions.

**7. Conclusions**

The two different laboratory test protocols used this study have shown that coal mine rock materials, particularly shales, ferruginous sandstones and coal preparation refuse, may interact with coal ash leachates and reduce the dissolved concentrations of several environmentally significant trace elements below those released from the ash in simple ash-water systems. An implication of these findings is that the concentration of at least some potentially significant trace elements released into percolating groundwater from a mine-site ash deposit may be attenuated by contact of the ash leachate with the adjacent rock strata. The extent of attenuation was greatest for those rocks with high proportions of clay minerals (e.g. shales) or Fe oxy-hydroxides (e.g. iron-stained...
sandstones). Rocks with lower clay or iron mineral contents, such as white quartz sandstones) appear to have a lesser attenuating effect.

Consideration of the various possibilities suggests that the principal mechanism responsible for the attenuation effects is adsorption by Fe oxy-hydroxides or clay minerals in the rock strata. The strong attenuation of elements likely to be released from the ash as oxy-aniions, such as Mo, As, and Se, in the neutral to mildly acid pH conditions developed in the present study, is consistent with such adsorption processes. Because the pH of the leachates in all of the materials tested varies over only a narrow range, precipitation effects associated with changing pH conditions are unlikely to be involved, at least for the ashes and rocks used in this particular program. Precipitation due to interaction with other ions (e.g., Cu), or ion exchange associated with the clay minerals may, however, also be involved, but only to a minor extent.

The serial batch test procedure is thought to indicate the attenuation that might take place when leachate from the ash migrates into the surrounding rock strata, including fragmented overburden rocks in other parts of the backfill. It also provides a more definitive basis for identifying the attenuation effects of different rock materials on a given ash leachate than the mixed batch test procedure. The mixed batch procedure is a complementary routine that may provide an indication of the leachate produced where ash and rock are more intimately mixed with each other in the backfill emplacement.

Although the most appropriate test program for any individual site will depend on the design and setting of the backfill operations, collection and evaluation of data from one or both procedures, in conjunction with regional hydrogeology and other site investigations, may be of value in assessing the environmental impact of particular ash placement options. Integration of such studies with larger-scale tests and on-site monitoring should also be undertaken, to test the findings more fully under field conditions.

8. Acknowledgements

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9. References


