Laboratory Evaluation of the Treatment of Alkaline Leachate with Coal Washery Discard

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Summary This paper presents a laboratory investigation into the utilisation of a New South Wales coal washery discard (CWD) as an inexpensive and readily available material for reducing groundwater alkalinity in situ. It is part of a larger study examining the potential for Australian CWD to be used as a permeable reactive barrier material for the removal of various inorganic and organic contaminant species from groundwater. Batch test results indicate that both fine and coarse CWD can reduce the pH of an alkaline contaminant solution from pH 11-12.5 to pH 8.5. The geochemical equilibrium model MINTEQA2 has been used to assist in the identification of the major attenuation mechanisms. It appears that the kaolinite and siderite within the CWD are dissolving and relatively insoluble secondary minerals (aluminium and iron hydroxides) are being formed. This process is time-dependent, and requires a higher residence time for contaminant solutions with a higher initial pH. Results indicate that CWD has the potential to be an economical and environmentally sustainable groundwater treatment material.

1 INTRODUCTION

Coal washery discard (CWD) is composed of high ash rock that was interbedded with, or was adjacent to, the coal prior to its extraction. It is separated from the coal during the washing stage of coal processing. Approximately 25 million tonnes of CWD were produced within New South Wales, Australia, during 1997-98. Since NSW has 7810 million tonnes of recoverable coal reserves and is currently producing coal at almost 108 million tonnes per year, the production of coal and CWD is likely to continue for many decades.

The primary disposal option for CWD is surface or near-surface emplacement (Wangen and Jones, 1984). This method requires large land areas and has the potential to result in surface water and groundwater contamination. Fluidised-bed combustion is growing in application and is discussed by Duffy and Kable (1984). It is therefore necessary to develop new options for the environmentally sustainable disposal of CWD. This paper is part of a larger study examining the use of Australian CWD as a permeable reactive barrier material for the in situ removal of inorganic and organic contaminants from groundwater. The use of a waste material in reactive barriers is likely to be cost-effective and reduces the demand for emplacement areas.

This paper focuses on a laboratory investigation into the neutralisation of alkaline groundwater at a blast furnace slag (BFS) emplacement using coarse Illawarra CWD. The aim is to quantify the neutralisation process and identify the primary attenuation mechanisms. Geochemical modelling with MINTEQA2, developed at the U.S. Environmental Protection Authority (Allison et al., 1991), has been performed to assist in this investigation.

2 CONTAMINANT SOLUTION

The alkaline contaminant solution has been taken from a BFS emplacement situated south of Wollongong, NSW, Australia. Table 1 gives the chemical characteristics of this groundwater. Column three of Table 1 lists some chemical characteristics of a sample of this groundwater which has been treated with acid to reduce the pH for purposes of this study.

It can be deduced from the data in Table 1 that the groundwater is saturated or nearly saturated (depending upon rainfall levels) with calcium hydroxide ($Ca(OH)_2$). This forms from the dissolution of calcium oxide (CaO) in the BFS. Since the emplacement is within a coastal marine aquifer, halite ($NaCl$) also dominates the groundwater chemistry.

During high intensity rainfall, this alkaline plume flows into a natural canal at the emplacement site and discharges into a stormwater drain. The drain flows into Lake Illawarra, which is a sensitive estuarine environment. In an attempt to prevent the movement of high pH water into Lake Illawarra, the canal has been filled with 6000 tonnes of local Illawarra coarse CWD to act as a permeable reactive barrier. Refer to Gray et al. (1999) for more detail regarding this CWD reactive barrier.

Table 1. Quality of the BFS groundwater.

Parameter	Groundwater taken from emplacement	Sample treated with acid
pH	12.70	11.14
conductivity (μs/cm)	6870	1684
calcium (Ca)	450	100
magnesium (Mg)	0.93	0.35
sodium (Na)	370	*
potassium (K)	29	*
iron (Fe)	0.2	2.2
aluminium (Al)	0.6	1.3
manganese (Mn)	0.01	*
zinc (Zn)	0.26	*
alkalinity as $CaCO_3$	486	82.5
chloride	300	*
sulphate	24.7	*

(all units mg/L except pH and conductivity)
* not measured

3 COAL WASHERY DISCARD PROPERTIES

The CWD used in these tests came from the South Bulli Colliery, which is part of the NSW Illawarra/Southern coalfield. Coal from this region is extracted from the Illawarra Coal Measures (approximately 200 metres thick on average), which is overlain by sandstones, shales and conglomerates and underlain by basalts, shales and sandstones. The larger study is also investigating the attenuation properties of CWD from the other four coalfields throughout NSW (Newcastle, Hunter, Western/Lithgow and Gunnedah) as well as from coalfields throughout Queensland.

Several tests have been conducted on the Illawarra CWD samples including particle size distribution, mineral content, and leachate composition.

3.1 Particle Size Distribution

CWD is produced as either a coarse rock-like material or as fine slurry (or tailings) depending on the processing mechanism. Coarse reject usually contains particles of size 0.5-127 mm, and fine reject is composed of particles of size <0.5 mm. According to McGlinn (1992), coarse reject can be divided by size into 'medium' (0.5-12.7 mm) and 'coarse' (12.7-127 mm). This study focuses on the attenuation capacity of coarse CWD since it is necessary that the reactive barrier is highly permeable.

At the macroscopic level, coarse Illawarra CWD is composed of carbonaceous shale and mudstone, sandstone fragments, ironstone, sand-sized particles and a small proportion of fines. Typical particle size distributions are given in Figure 1. On average, this CWD is composed of approximately 84% gravel and cobbles, 15.5% sand-sized particles and only 0.5% silt/clay sized particles. Note that both coarse samples contain a small amount of fines (about 4%).

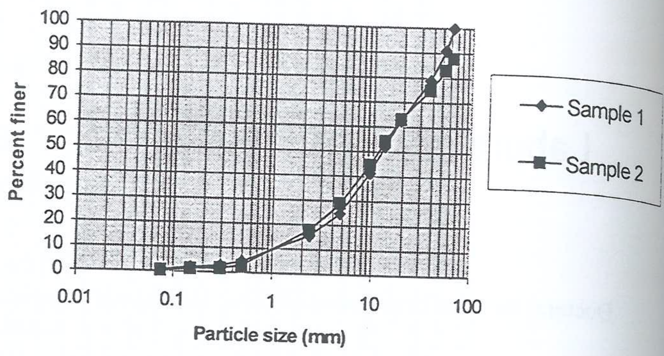

Figure 1. Particle size distribution for coarse Illawarra CWD.

Reactive barriers must be permeable to allow groundwater to pass through them so that contaminants in the water can react with the media within the barrier. However, if the hydraulic conductivity of the barrier is too high, the residence time may be insufficient. Of course, if the hydraulic conductivity is too low, then the groundwater may flow around the barrier. Column testing (described by Shackelford, 1994) will be used to investigate the relationship between contact time and pH reduction.

3.2 Mineral Content

X-ray diffraction analysis was used to identify the mineral phases present in the CWD. Each analysis identified quartz (SiO_2), kaolinite ($Al_2Si_2O_5(OH)_4$), siderite ($FeCO_3$), calcite ($CaCO_3$) and illite ($KAl_2(Si_3AlO_{10})(OH)_2$) as the major mineral components of CWD. As shown by Figure 1, most of these minerals are within gravel-sized particles. Unlike the CWD produced in many other areas of the world, Illawarra CWD contains very small quantities of acid producing pyrite. According to Ward (1980), siderite forms in coals and other organic sediments that do not contain pyrite, due to the lack of sulphur compounds.

Short et al. (1998) has also studied CWD from the South Bulli Colliery, and the mineral composition of CWD according to this study is given in Table 2.

Table 2. Mineralogy of South Bulli CWD (adapted from Short et al., 1998)

Mineral	% by mass
Quartz	25
Clay minerals (kaolinite, illites, chlorites)	35
Siderite	5-10
Calcite	2
Carbon/fine coal	20-30

CWD has the potential to remove various organic and inorganic species from groundwater. Its high carbon content may make it a viable option for the treatment of harmful organic species such as phenol, benzene and toluene. In addition, the clay minerals may remove trace heavy metals from groundwater via cation exchange processes, while the carbonates provide a neutralisation capacity.

3.3 Leachate Composition

Neutralisation of pH is achieved by the interaction of the contaminant solution with the mineral species present. Several studies have examined the leaching behaviour of CWD, including Ward (1980), Kerth and Wiggering (1990) and McGlinn (1992). In each of these studies, soluble components were extracted from the CWD using an acidic solution.

When Illawarra CWD is subject to a standard leaching test, a leachate of pH 8.5-9.5 is produced. According to McGlinn (1992), calcium and magnesium are the major cations in this alkaline solution. Iron and aluminium are present in lower concentrations. It is most likely that this pH rise is due to partial dissolution of the carbonates calcite ($CaCO_3$) and siderite ($FeCO_3$). Since dolomite ($(Ca,Mg)CO_3$) was not identified from X-ray diffraction, it is most likely that the magnesium present in the leachate is derived from a magnesium-bearing siderite (McGlinn, 1992).

It cannot be assumed that these CWD minerals will behave in the same way under highly alkaline conditions. Indeed, one would expect that most of the minerals would be much less soluble when exposed to the BFS leachate.

4 LABORATORY TESTING

No standard method could be found for measuring the neutralisation capacity of the Illawarra CWD. Hence, the standard method for a short-term batch test, ASTM D 4319-93 (ASTM, 1997), was used. Conventional batch tests are used to establish an adsorption isotherm for a contaminant/soil combination. This method assumes that contaminant attenuation from all other reactions - precipitation and oxidation-reduction - is negligible. In this case, it is reasonable to assume that any pH reduction is due to reactions between the multicontaminant solution and aqueous species leaching from the CWD. Ion exchange and adsorption processes may be taking place, however these are likely to have a smaller impact on solution pH than mineral dissolution.

A sample of coarse Illawarra CWD was first dried in the oven to remove non-structural moisture and then crushed to a maximum particle size of about 10 mm for small-scale laboratory testing purposes. A portion of the crushed coarse CWD was then passed through a 500 µm sieve to obtain a sample of fine reject (<0.5 mm). For both the coarse and fine fractions, 5 g, 10 g, 20 g and 25 g samples were combined with the pH 11.14 multicontaminant BFS groundwater solution (Table 1) in a solution volume (mL) to CWD mass (g) ratio of 4:1. The BFS groundwater was treated with acid so as not to harm the calcium ion selective electrode used for instantaneous calcium monitoring. Each reaction flask was then shaken on a laboratory shaker for 6 hours for every 3 day portion of the contact period. The contact period ranged from 1 day to 13 days. At the end of each contact period, the supernatant was separated from the solid phase and filtered before analysing for pH, conductivity, calcium, magnesium, iron, aluminium, alkalinity and carbonate using the appropriate standard analytical method described in APHA (1985).

In addition, to assist in the identification of the major attenuation mechanisms, 20 g samples of oven-dried quartz sand, oven-dried kaolinite clay, pure calcite and coarse CWD were combined with the pH 12.59 contaminant solution (Table 1). Siderite is not available in pure form, and therefore could not be included in this test. The standard method procedure was used to monitor any pH change over time.

5 BATCH TEST RESULTS

Figure 2 compares the pH reduction over time for the 5 g, 10 g, 20 g and 25 g coarse CWD samples. In each case, the pH reduces to about 8.3 - 8.8 after three days and converges to 8.5 after 13 days. This similar pH reduction pattern is due to the contaminant solution to CWD ratio being the same in each case.

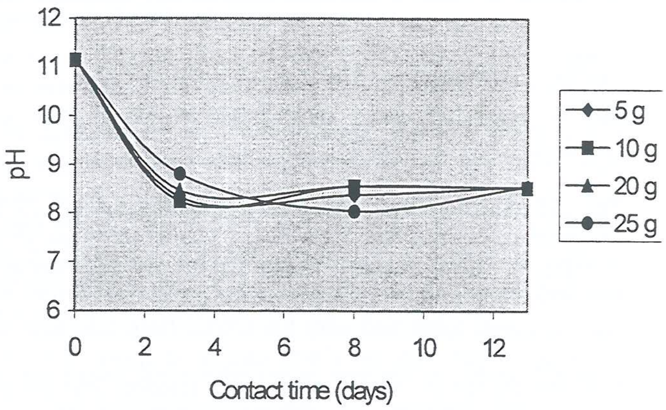

Figure 2. pH reduction for coarse CWD samples.

The pH reduction over time for a 20 g coarse CWD sample and a 20 g fine CWD sample is given in Figure 3. Coarse and fine CWD have a similar pH reduction pattern. Note, however, that the reduction rate is greater for the fine CWD during the first few days. This is most likely due to the greater surface area within the fine sample and the greater initial mineral dissolution. Over time, an equilibrium pH of about 8.5 is reached in each case.

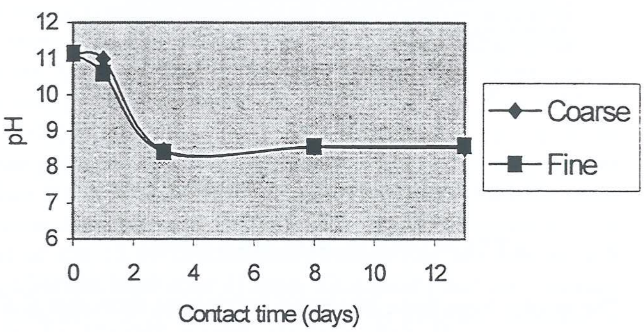

Figure 3. pH reduction for 20 g samples.

Other groundwater quality parameters were monitored in addition to pH (Table 3). Again, it is necessary to show the changes for only one CWD mass.

Table 3. Changes in contaminant solution chemistry for 20 g CWD samples.

Analyte	Initial Level	Coarse CWD			Fine CWD		
		3 d	8 d	13 d	3 d	8 d	13 d
pH	11.14	8.49	8.55	8.54	8.41	8.57	8.6
cond (μS/cm)	1684	1708	1785	1877	1752	1782	1854
CO_3^{2-}	12.8	-	-	-	-	-	-
HCO_3^-	-	70.14	88.57	102	73.28	94.78	103.3
Ca^{2+}	100	30.43	44.13	29.42	47.61	55.01	66.67
Mg^{2+}	0.35	2.06	2.32	2.13	3.95	4.63	4.96
Fe^{2+}	2.2	1.45	1.77	0.59	0.95	0.33	0.49
Al^{3+}	1.3	1.74	0.74	1.03	2.7	1.33	0.81

(all units mg/L except pH and conductivity)

As shown in Table 3, electrical conductivity increases over time for both the fine and coarse samples. This indicates that minerals within the CWD are gradually dissolving in the alkaline environment. In each case, there is a net increase over time in magnesium, and a net decrease in calcium, iron and aluminium.

The pH reductions resulting from combining the pH 12.59 contaminant solution with individual CWD minerals are given in Figure 4. This data clearly shows that the pH reduction with kaolinite alone is much greater than the pH reduction with the other minerals alone and with the CWD. Note also how the reduction in pH with the CWD sample is slower than that observed for the pH 11.14 contaminant solution. The pH has only reduced to 9.7 after 11 days of contact. These results will be explained in the following section.

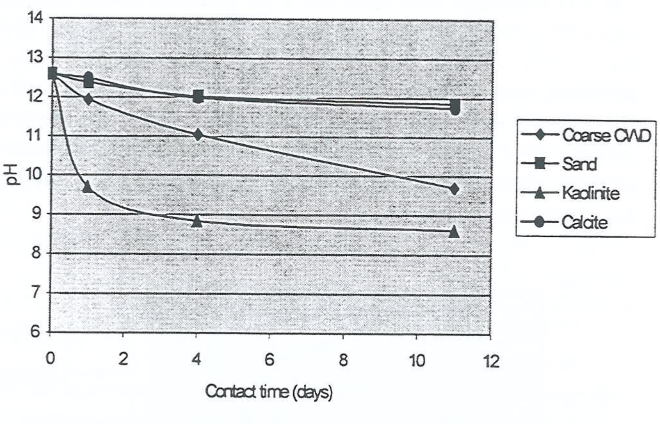

Figure 4. pH reduction for individual minerals.

6 ATTENUATION MECHANISMS

The results from these laboratory batch tests show that CWD can reduce the pH of alkaline groundwater. This pH reduction is caused by the interaction between certain minerals within the CWD and the alkaline species in the BFS groundwater. The equilibrium geochemistry model MINTEQA2 has been used to aid in the identification of the major attenuation mechanisms.

6.1 Hydroxide Formation

The primary mechanism which leads to this pH reduction is most likely to be the dissolution of siderite and kaolinite from the CWD and the formation of secondary minerals: ferrous hydroxide ($Fe(OH)_2$), ferric hydroxide ($Fe(OH)_3$) and aluminium hydroxide ($Al(OH)_3$) precipitates. The formation of the iron precipitates is given by (1) and (2) and the formation of the aluminium precipitate is given by (3) and (4). Ferrous hydroxide is readily oxidised in air to form ferric hydroxide. Unfortunately, ferric hydroxide tends to have a positive total net surface charge and often coats the negatively charged surfaces of many soil particles (Fryar and Schwartz, 1994). This coating may hinder further dissolution of siderite and could also reduce the hydraulic conductivity of a reactive barrier.

$$FeCO_{3(aq)} + Ca(OH)_{2(aq)} \Leftrightarrow Fe(OH)_{2(s)} + Ca^{2+} + CO_3^{2-} \quad (1)$$

$$2FeCO_{3(aq)} + 3Ca(OH)_{2(aq)} \Leftrightarrow 2Fe(OH)_{3(s)} + 2e^- + 3Ca^{2+} + 2CO_3^{2-} \quad (2)$$

$$Al_2Si_2O_5(OH)_{4(s)} + 6H^+ \Leftrightarrow 2Al^{3+} + 2H_4SiO_{4(aq)} + H_2O \quad (3)$$

$$2Al^{3+} + 3Ca(OH)_{2(aq)} \Leftrightarrow 2Al(OH)_{3(s)} + 3Ca^{2+} \quad (4)$$

This attenuation mechanism can also explain the changes in solution chemistry shown in Table 3. The consistent increase in magnesium can be attributed to the dissolution of a magnesium-bearing siderite. Magnesium does not form a hydroxide since $Mg(OH)_2$ is considerably more soluble than the aluminium and iron hydroxides. The level of calcium reduces due to additional carbonate ions entering into solution from the dissolution of siderite and the resulting precipitation of calcite. In addition, there is a net decrease in aluminium and iron due to the formation of the hydroxides. Since the concentrations of most of the measured species are decreasing, the increase in solution conductivity implies that other unmeasured species are entering into solution.

Results from X-ray diffraction analysis confirm that the formation of the aluminium and iron precipitates is the most likely attenuation mechanism. A significant drop in the intensity at 2θ = 12.33 and 24.84 (kaolinite peaks) and 2θ = 32.05 (siderite peak) was observed for the coarse Illawarra CWD after 11 days batch testing. In addition, a significant drop in the intensity at the kaolinite peaks was also observed for the kaolinite clay after 11 days batch testing. This indicates that the kaolinite and siderite are partially dissolving and releasing Al^{3+} and Fe^2+ ions that are able to react with the

OH^- ions. It should be noted at this stage that although the dissolution of siderite and kaolinite is favoured by acidic conditions, dissolution at pH 11-12.5 is sufficient to remove most of the hydroxide from solution. Kau et al. (1996) reports that kaolinite dissolution and the release of Al^{3+} ions is least at approximately pH 7 and increases marginally under basic conditions.

This attenuation mechanism has been simulated using MINTEQA2. The model incorporates the initial concentrations of various species within the BFS groundwater and the mineral phases added when the contaminant solution is mixed with the CWD. It was assumed that the CWD is 15% kaolinite and 10% siderite by mass, as given in Table 2. In this way, a 20 g sample in 80 mL of solution contains 0.2 mol/L kaolinite and 0.216 mol/L siderite. The MINTEQA2 output is summarised in Table 4.

Table 4. MINTEQA2 output at equilibrium.

Parameter	MINTEQA2 output
equilibrium pH	8.28
kaolinite	0.1999 mol/L
siderite	0.2016 mol/L
aluminium hydroxides/oxides formed (gibbsite, diaspore)	5.9×10^{-5} mol/L
iron hydroxides/oxides formed (wustite, ferrihydrite)	1.4×10^{-2} mol/L

The predicted pH reduction using MINTEQA2 is reasonably close to the actual reductions measured for the pH 11.14 contaminant solution (Figure 2 and Figure 3). However, it is substantially lower than the pH recorded after 11 days contact between the pH 12.59 contaminant solution and the coarse Illawarra CWD (Figure 4). Since MINTEQA2 is an equilibrium model, it does not incorporate reaction kinetics. Rather, it assumes that all reactions proceed instantaneously. In this case, the dissolution of kaolinite and siderite is slower at higher initial pH, resulting in a slower pH reduction. Although the pH for the CWD sample in Figure 4 will eventually converge to about pH 8.3-8.5, it takes longer than the samples in Figure 2 and Figure 3.

Note also from Table 4 that the dissolution of siderite is greater than the dissolution of kaolinite, and the formation of iron hydroxides is far greater than that for aluminium. Therefore, based on the MINTEQA2 output, the formation of iron hydroxides is the dominant pH reduction mechanism when a sample contains both siderite and kaolinite. This could be explained by the fact that ferric hydroxide is more insoluble than aluminium hydroxide. However, this result seems to contradict the data in Figure 4 that shows how kaolinite alone provides a greater pH reduction than kaolinite and siderite combined. This will require further investigation.

6.2 Silica Dissolution

Another attenuation mechanism that has been considered is silica dissolution. The dissolution of silica is favoured by alkaline conditions, and results in the generation of H^+ as shown by (5).

$$SiO_{2(s)} + 2H_2O \Leftrightarrow H_4SiO_{4(aq)} \quad (5)$$

Short et al. (1998) believes that the dissolution of silica can have a neutralising effect on alkaline solutions. However, Figure 4 indicates that the process in (5) is very slow and has only a very small impact on solution pH within the first 11 days of contact. MINTEQA2 predicts that the pH will reduce from 12.5 to 10.33 when silica interacts with the alkaline solution. However, recall that MINTEQA2 assumes that all reactions proceed to completion instantaneously. Therefore, although the pH may eventually reach 10.33, this may take weeks or months in the laboratory.

Since the CWD is to be used as a reactive barrier material, contact time is limited and may become particularly low during times of high rainfall. Hence, although silica can theoretically reduce the pH of an alkaline solution in the long term, it would not necessarily be the dominant pH reduction mechanism within a reactive barrier.

7 CONCLUSIONS AND RECOMMENDATIONS

The development of new utilisation options for CWD is a growing area since millions of tonnes of this waste rock material will continue to be produced annually within New South Wales. This paper is part of a larger study investigating the potential for CWD to be used as a permeable reactive barrier material for the in situ removal of various organic and inorganic contaminant species from groundwater.

In this paper, the neutralisation capacity of coarse Illawarra CWD has been examined. Based on a laboratory batch testing programme, it appears that CWD is capable of reducing the pH of highly alkaline groundwater saturated with $Ca(OH)_2$. An equilibrium pH of about 8.5 was reached within about three days for both the fine and coarse CWD samples when the initial contaminant solution pH was 11.14. However, when the CWD was combined with the pH 12.59 contaminant solution, the pH had reduced to only 9.7 after 11 days of contact.

It appears that the primary mechanism reducing the pH is the dissolution of kaolinite and siderite from the CWD and the formation of aluminium and iron hydroxides. X-ray diffraction analyses highlight this gradual dissolution in kaolinite and siderite during batch testing. The MINTEQA2 geochemical model has been used to simulate this process. Based on this model, the equilibrium pH is about 8.2-8.3 regardless of the initial contaminant solution pH. This value is similar to the final pH measured in the laboratory for the pH 11.14 solution since it had already reached equilibrium. However, due to the slower dissolution of kaolinite and siderite in higher pH, the pH of the 12.59 contaminant solution had not reached this equilibrium level after 11 days. This means that the hydraulic conductivity of a CWD reactive barrier must be optimised so that the residence time is sufficient to neutralise the highest pH to be expected in the field.

Silica dissolution was found to be negligible, despite the alkaline conditions. Although silica may theoretically dissolve in the long term to produce an acidic solution, contact times are limited within a reactive barrier. Therefore, the contribution by silica to the total pH reduction would be negligible.

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