

Regulatory implications low pH coal combustion products Australian perspective

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ABSTRACT

Low pH coal combustion products (CCPs) of less than 7 pH units are considered unsuitable for land application in civil projects within selected jurisdictions. Traditional methods used to determine pH in CCPs could provide misleading risk assessments. Using acid sulfate soil (ASS) methodologies we quantified net acidity and therefore risk, and submit this is a valid proposition with which to interpret risk with use of CCPs for land applications. We propose that risk of acidity potential to the surrounding environment when quantified by values derived from either a chromium reducible suite or a SPOCAS assessment can confirm a low risk or no risk. We suggest that identifying sulfur-based acidity identifies the low risk of sulfidic acidity for coal ash materials generally, which is a correct representation for the oxidation process of coal combustion. By SPOCAS analysis, we identified that a low pH CCP of less than pH 7 was not generally indicative of a net acidic risk potential. The implication of this method of assessment to regulatory exemptions, in the context of application to land under various state regulations and approvals, is this is more informative than a determination of pH value. Another investigation mixed low pH CCPs with acidic and alkaline quarried materials to evaluate the overall pH of the combined materials at various percentages. The results confirmed that low pH CCPs when blended with alkaline road base it remained alkaline. Where CCPs were blended with commercially used acidic road base it remained acidic. It can be concluded that the pH nature of a road base was the key determining factor, suggesting low pH CCPs had little or no influence on the resultant pH of the road base material. This paper discusses these risks in the context of application to land as part of General Exemptions and Approvals granted under various Australian State legislation and regulations.

INTRODUCTION

Low pH values for a coal ash have been reported as a common property for many of Australian black coals (Jankowski *et al.* 2006). Correspondingly the coal combustion products¹ (CCPs) of those black coals, also with low pH have been considered as materials unsuitable for land application in civil projects (NSW EPA 2010). State regulatory restriction is a blanket at-source limitation to the development potential of using CCP's in civil construction and particularly for various civil and structural engineering, road base, pipe and embankment applications (ADAA 2005). Consequently, research and investigation was undertaken to better understand how risks could be quantified within the chain of responsibilities (supplier, processor and consumer) that are defined within existing General Exemptions².

BACKGROUND

In 2011 the Ash Development Association of Australia (ADAA) as part of its annual Environmental Monitoring Program (EMP) expanded its normal suite of assessments for pH, electrical conductivity and metal elements (As, Sb, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Se, Ag, V, Zn), with an inclusion of alkali metals (Ca, Mg, K, Na); P and S, soluble elements Cl^- , SO_4^{2-} and B (CaCl_2 extractable) and analysis assessment used to identify acid sulfate soil (ASS).

Our hypothesis was that CCPs defined as 'low pH' could be better understood using methodologies of analytical assessment and interpretation, as developed for Acid Sulfate Soils (ASS). The data collected using these methods would be an informative model and demonstrated that acidic properties of the low pH CCPs could be quantitated and therefore risks evaluated.

Selected Australian sources of CCPs are known to have low pH ranges and in some cases low pH buffering capacity (Ward *et al.* 2009; Janowski *et al.* 2006). With an elemental composition predominately quartz, mullite and glass with smaller quantities of hematite, magnetite, maghemite and cristobalite (Ward and French 2006), and some ash containing gypsum, anhydrite, portlandite, lime, calcite, hannebachite, sillmanite and rutile (Kutchko and Kim 2006), the CCPs, and particularly fly ash, has concentrations of trace elements that vary with coal source and that can be higher than the equivalent concentrations in the coal source. This concentration of trace elements is described by Jankowski *et al.* (2006) as enrichment, condensed on the particle surfaces in the furnace atmosphere Ward *et al.* (2009).

The mobility of these enriched trace elements from coal combustion products when demonstrated under leaching conditions has long been associated with the pH developed within the ash-water system (Ward *et al.* 2009). Change in acidity has been identified as a process related to sulfate condensed on the particle surfaces (Brownfield 2002) that is thought to pass into solution as sulphuric acid initially lowering the pH of the ash-water system (Roy and Griffin, 1984; Sear *et al.* 2003). Then in many cases where a CCP particle surface contains high proportions of CaO

¹ Coal combustion products include fly ash (FA), furnace bottom ash (FBA), boiler slag (BS), fluidized-bed combustion (FBC) ash, or flue gas desulfurization (FGD) material produced primarily from the combustion of coal or the cleaning of the stack gases. The term coal ash is interchangeable

² <http://www.environment.nsw.gov.au/resources/waste/CoalAshExemption2011.pdf> (accessed Jan 2013)

(or alkalis and alkaline earth elements in relation to SO_3) a low pH is only a transient situation, and the pH rises rapidly as calcium also passes into solution from deeper layers on the particle surface (Ward *et al.* 2009).

An acid sulfate soil assessment is a model that was developed for the purpose of identifying a quantitative risk for soil typically waterlogged and rich in pyrite which has not been oxidised. Any disturbance exposing these soils to air (oxygen) can lead to the development of extremely acidic soil layers or horizons with field pH values of <4, and actual acid sulfate soils (Ahern *et al.* 2004). Evaluation of these soils is by measuring reduced inorganic S compounds in soils and sediments using a chromium reduction method (chromium suite) (Sullivan *et al.* 2004) or with the suite of tests called Suspension Peroxide Oxidation Combined Activity and Sulfur (SPOCAS) (McElnea *et al.* 2002). Both methods (SCR and SPOCAS) derive a value of net acidity as an acid based account also known as the acid trail which includes an initial measure of titratable actual acidity (TAA). The Titratable Actual Acidity or TAA (the first component of the 'acidity trail') is a measure of the soluble and exchangeable acidity already present in the soil, often as a consequence of previous oxidation of sulfides. It is this acidity that will be mobilised and discharged following a rainfall event (Ahern *et al.* 2004).

Additional to a TAA value are the investigations that will identify organic and inorganic sulfur based acidity. The Chromium Reducible Sulfur (SCR) method provides accurate, low-cost determinations of (non-sulfate) inorganic sulfur and is not subject to significant interferences from the sulfur, either in organic matter or sulfate minerals such as gypsum (Sullivan *et al.* 2004) and the preferred technique for estimating acid-producing inorganic sulfur in ASS, particularly near the action limits and on organic-rich samples (Ahern *et al.* 2004). Alternately, the evaluation based on SPOCAS methodology also interprets acidity with acidity units of mol H^+ /t but includes measurement of peroxide sulfur to allow calculation of peroxide oxidisable sulfur (SPOS) in order to identify the presence of other sulfate salts with no acid-generating potential (such as gypsum), sulfur from the oxidation of organic matter, as well as that derived from sulfides. The complete SPOCAS method provides 12 individual analytes (plus 5 calculated parameters), enabling the quantification of some key fractions in the soil sample, leading to better prediction of its likely acid-generating potential. Put most simply, the SPOCAS method involves the measurement of pH, titratable acidity, sulfur and cations on two soil sub-samples. One soil sub-sample is oxidised with hydrogen peroxide and the other is not. The differences between the two values of the analytes from the two sub-samples are then calculated (Ahern *et al.* 2004).

The testing with CCPs using the SPOCAS model applies an analytical methodology to measure acidity with acidity units of mol H^+ /t and includes an interpretation for soluble and exchangeable portions in solution. It was assumed this methodology would be applicable to a wide range of CCP sources and variability.

Coincident with this characterisation study using industry accepted methods of assessment to identify acid sulfate soil (ASS) one power station situated in New South Wales commissioned an independent investigation into pH of CCPs and road base blends. The aim was to evaluate sources in combination with acidic or alkaline road base blends and to confirm their initial and stabilized pH values with various percentage mixes and demonstrate that the buffering capacity of the CCPs was less

than the natural material blends. Whilst both low and high pH materials were evaluated, low pH CCPs results will be discussed given the focus of the paper.

METHOD/S

Acid Sulfate Soil Analysis by SPOCAS

Annually, the Ash Development Association of Australia³ collects, submits for assessment and publishes the findings within an Environmental Monitor Program Report (EMP) of members' CCPs. EMP assessments were first conducted in 2003. The aim of the EMP is to collate and interpret the analytical knowledge on its members' CCPs through a coordinated annual sampling, analysis and reporting program. During the 2011 program seventy two (72) samples collected using methods defined in AS1141-3.1 Methods for sampling and testing aggregates (Standards Australia 1996) were submitted for chemical analysis including total concentrations of heavy and alkali metals and salts of B and S. Standard moisture content (%), conductivity (uS/cm) and pH tests (1:5) were also undertaken. Sixteen (16) samples were then submitted for SPOCAS assessment selected from eight (8) sources on the basis of acid and or alkaline fly ash.

SPOCAS testing was undertaken on the basis of (Rayment and Lyons 2011 and Ahern *et al.* 2004) by the NATA registered environmental laboratories MGT Labmark, Sydney, NSW). TAA solutions were prepared with a 1:40 soil and KCl solution for the measure of titratable actual acidity (TAA) For the second assessment by SPOCAS the ash sample was oxidized with hydrogen peroxide and the pH and acidity of that solution recorded. This test was called titratable potential acidity (TPA). Also known as titratable peroxide acidity, the TPA represents the amount of acid released from the complete oxidation of sulphides, organic matter, pre-existing TAA and any buffering provided by acid neutralising components in the soil. The difference between TPA minus TAA is titratable sulfidic acidity (TSA). All results were expressed as acidity units of mol H⁺/tonne and a net value of acidity was calculated.

Comparisons discussed in this paper were between standard pH, TAA (mol H⁺/tonne), total Ca%, total Mg%, total S%, SO₄²⁻ net acidity (mol H⁺/tonne), liming capacity (kg CaCO₃/t) and S_{POS} %.

Road Base Blends

For the investigation into pH of CCPs and road base blends, CCPs were blended with a range of road base materials to identify changes in pH following the blending process. Three commonly available road bases were evaluated;

- (i) two natural quarried sources were alkaline and
- (ii) one natural quarried source acidic in nature.

The following Table 1 show the pH values for three natural quarried sources.

³ <http://www.adaa.asn.au/environmental-monitoring-reports.php>

Quarry Source	Product type	pH Reading	Comments
Kulnura Basalt	<2.36mm minus	9.4	Highly alkaline
Marangaroo Quartzite	<2.36mm minus	4.1	Acidic
Hyrock Limestone	<2.36mm minus	8.3	Moderately alkaline

Table 1 – Unblended Road Base (fine aggregate)

Low pH ungraded⁴ fly ash was blended in different ratios with each of the three road bases. Rates of addition ranged between 5% to 25% ash content in the road base blend. Table 2 shows the blended proportions evaluated.

Aggregate tested	Wallerawang Run of Station (ROS) Fly Ash at Nominated Addition Rates		
	5% Ash	10% Ash	25% Ash
Kulnura Basalt	95	90	75
Hyrock Limestone	95	90	75
Marangaroo Quartzite	95	90	75

Table 2 – Blending Proportions with low pH fly ash

RESULTS

Assessment of Road Base Blend

The lowest pH of the 72 samples assessed was a fly ash with pH 3.4. The highest reported a pH 12. The fly ash assessed with pH 3.4 has historically been used in the road base blends without environmental incidence/s.

The buffering capacity of an acidic ash is a measure of the potential for the ash to produce acidic ions. In other words it indicates the extent to which an acidic material when mixed with a neutral material will continue to be acidic. Unlike Portland cement, low pH ashes do not have a high buffering capacity. As such when mixed with an alkaline road base material Kulnura Basalt with initial pH 9.4 the pH of the overall mixture remained alkaline at pH 8.7 (Table 3). Evident within this work is that addition rates of 25 % were needed to induce that reduction in pH value. Of interest is that the initial response to the alkaline road bases and acidic fly ash was a temporary increase of pH with blends at 10 % then at 25% the pH reduction was developed. Alternatively, an acidic road base material Marangaroo Quartzite with initial pH 4.1 developed more acidity a pH 4.0, irrespective of the blend percentages, as shown in Table 3. In this case the 5% ash blend to the Marangaroo Quartzite did not change the value of pH, which remained at pH 4.1. In all cases the acid fly ash resulted in a slightly lower pH when the incorporation was 25 %, which decreased at a lesser rate as pH values of the original material reduced. Figure 1 shows that only alkaline road base blends had a change in pH when blended with acidic fly ash.

⁴ Particle size distribution between 1 – 300 microns

Aggregate tested	pH of 100% road base	pH of blend containing Wallerawang ROS Fly Ash at Nominated Addition Rate		
		5% ash	10% ash	25% ash
Kulnura Basalt	9.4	10.2	10.1	8.7
Hyrock Limestone	8.3	8.3	8.5	7.9
Marangaroo Quartzite	4.1	4.1	4.0	4.0

Table 3 – Blended Road Base with low pH fly ash @ 5%, 10% and 25%

Figure 1 Graphical interpretation of change in pH units for different blend percentages of fly ash into road base. The original pH value of 100 % road base is also shown in the data table. At 5% and 10 % fly ash blended, there was only a positive or zero response. Only the alkaline fly ash induced a reduction of pH when the blend was 25%. There was no response or pH change in the acidic quartzite road base.

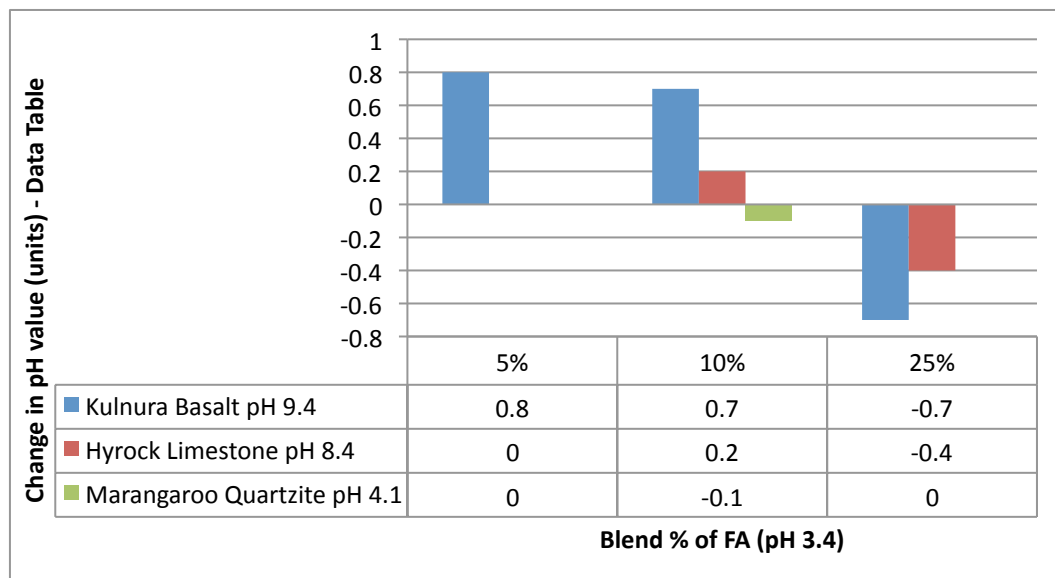


Figure 1 Graphical interpretation of change in pH units for different blend percentages of FA into road base.

Use of pH to identify acidity

Eight (8) FA and eight (8) FBA samples selected for the SPOCAS assessment were from power stations located in New South Wales, South Australia and Western Australia. The representative pH value of these coal ashes were between pH 3.4 to 12, with the lowest pH that was represented as the fly ash from the road base study. All furnace bottom ashes had pH values of 7 or above, except one (1) at pH 5.2. Six (6) of the eight (8) fly ashes had pH values below pH 7 with two (1) at pH 12 (Figure 2, 3 and Table 4).

Fly ash, when acidic, was observed to have lower pH than the furnace bottom ash from the same source power station and when alkaline and above pH 9.5, observed to be of higher pH than the furnace bottom ash. Consequently, from the same source power station fly ash and a furnace bottom ash is not a product with the same pH

characteristic. Comparative pH values of standard pH determinations are presented in Table 4 and graphed as shown in Figure 2.

Alternatively, and with relevance to the quantitation of acidity via the acid trail, the use of a standard pH can be shown to be indicative of the pH of dilute solutions (TAA) and peroxide solution (TSA) when the standard pH was below pH 7.0 (Figure 3). In this cases where the standard pH value was less than pH 7 TAA and TSA solutions would be correlated. Consequently, this relationship would support the use of an assessment of net acidity via the ASS acid trail methodology, in order to determine a risk for an environmental application being associated with a low pH CCP.

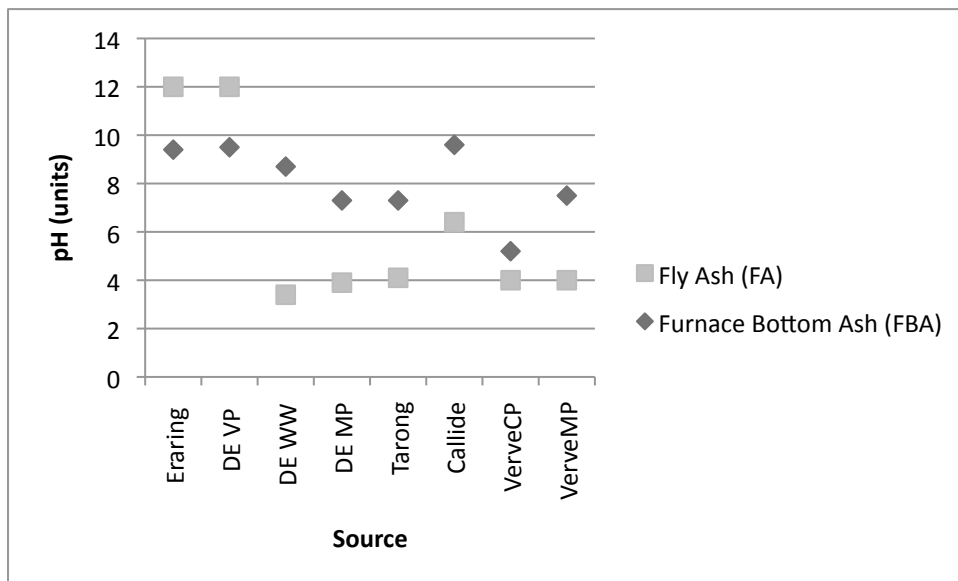


Figure 2 Graphic representation of FA and FBA pH (1:5_{standard}) for selected power stations in Australia in the study to assess use of acid sulfate soils SPOCAS methodology.

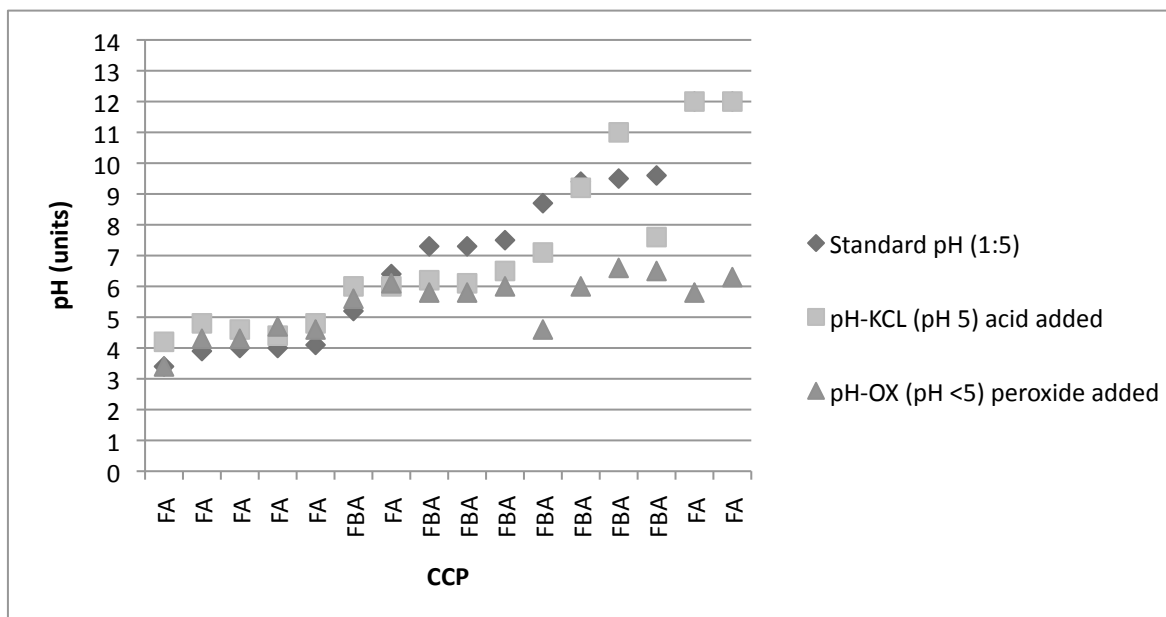


Figure 3 Graphic representation of pH solutions (standard, TAA, TSA) for FA and FBA of selected power.

Sulfur and Sulfate

Samples were assessed to confirm the relationship between sulfate (SO_4^{2-}), total sulfur (S) and the percentage S of the TAA solutions. In this study the relationship between total S and SO_4^{2-} values was $r^2 = 0.9447$. %S was negligible in furnace bottom ash at less than 0.02 %S. Percentages of SO_4^{2-} and the %S of the TAA solution was specific only to fly ash. Acidic fly ash at less than pH 4.0, had higher %S in the TAA than when $> \text{pH } 4.0$ (Figure 4).

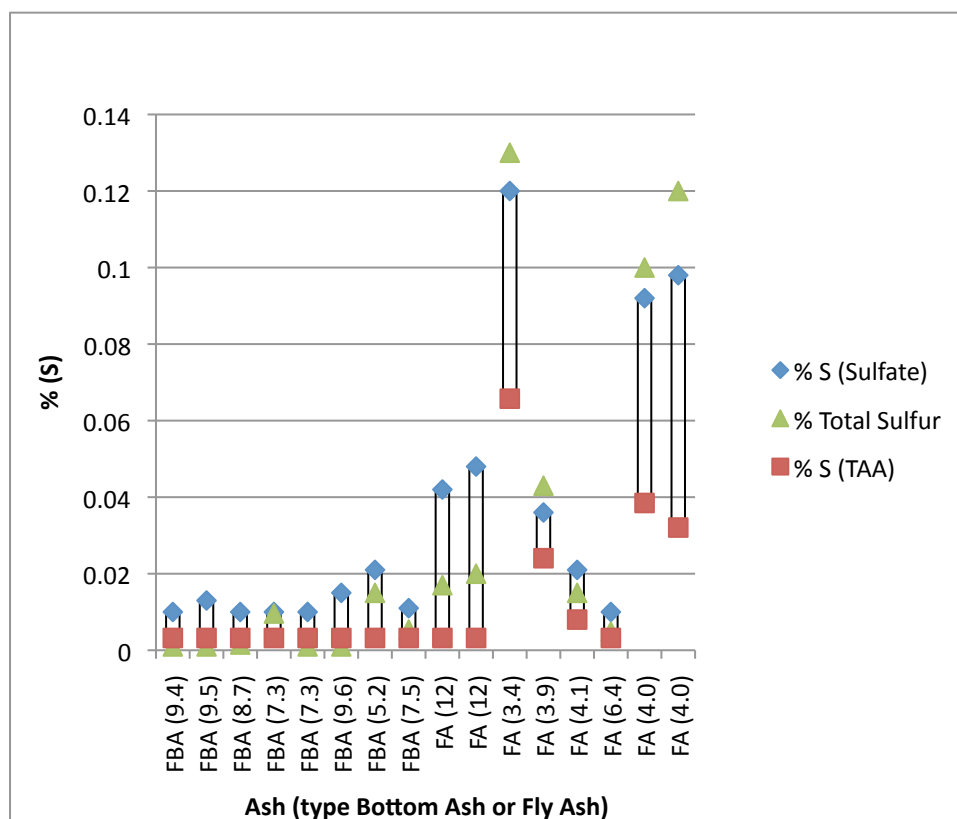


Figure 3: Plot of % values of S (sulfate, total S and TAA) for FBA and FA across pH range 3.4–12). Diamonds are %S (total, squares are %S of the TAA solution, triangles are % SO_4^{2-} .

Titrateable Actual Acidity and Peroxide Oxidised Solutions

Initial assessment of ASS properties was by comparison between the furnace bottom ash and fly ash as a plot of the values of TAA against pH values the standard pH test result at 1:5, the pH of the 1:40 KCl and the pH values of the oxidised solution (Figure 5). TAA ranged from 5 to 40 mol H^+/t only when below pH 5.0 (1:5). For ashes with pH values above pH 5.0 (1:5) the corresponding TAA was below the limit of detection at $< 2 \text{ mol H}^+/\text{t}$. Of interest is that the pH of the TAA and TSA solutions was slightly higher than the standard pH test result. Also, for ASS the action value as a management response is 18 mol H^+/t . Of interest is that the lowest pH of 3.4 had a soluble acidity value of 15 mol H^+/t and a pH value at less than pH 5.0 was not indicative of acidity above the ASS action value.

This comparison identifies (i) that TAA was only quantifiable and above detection limit when pH of the analytical solutions were below pH 5.0; (ii) a pH value of 5.0 or

9.5, even though for that sample the total %S was 0.013 %. The corresponding net acidity of 14 mol H⁺/t) also had the highest %Ca and %Mg.

Line	Source	Ash ^{1,2}	pH _(1:5)	Ca (%)	Mg (%)	Net Acidity (mol H ⁺ /t)	Lime kg CaCO ₃ /t	TOS (% S)	S _{POS} (%)	S (%)
1	DE WW	FA	3.4	0.042	0.014	42	3.2	0.07	<0.02	0.12
2	DE MP	FA	3.9	0.016	0.014	15	1.1	0.02	<0.02	0.036
3	Verve CP	FA	4	0.42	0.18	24	1.8	0.04	<0.02	0.092
4	Verve MP	FA	4	0.5	0.18	22*	1.6	0.03	<0.02	0.098
5	Tarong	FA	4.1	0.0019	0.0052	<10	<1	<0.02	<0.02	0.021
6	Callide	FA	6.4	0.035	0.036	<10	<1	<0.02	<0.02	0.01
7	Eraring	FA	12	0.89	0.06	<10	<1	<0.02	<0.02	0.042
8	DE VP	FA	12	1.1	0.11	<10	<1	<0.02	<0.02	0.048
9	Verve CP	FBA	5.2	0.046	0.018	<10	<1	<0.02	<0.02	0.021
10	Tarong	FBA	7.3	0.0073	0.0059	<10	<1	<0.02	<0.02	0.01
11	DE MP	FBA	7.3	0.0078	0.0029	<10	<1	<0.02	<0.02	0.01
12	Verve MP	FBA	7.5	0.031	0.011	<10	<1	<0.02	<0.02	0.011
13	DE WW	FBA	8.7	0.036	0.0095	<10	<1	<0.02	<0.02	0.01
14	Eraring	FBA	9.4	0.2	0.064	<10	<1	<0.02	<0.02	0.01
15	DE VP	FBA	9.5	0.97	0.32	14	1	<0.02	0.21	0.013
16	Callide	FBA	9.6	0.11	0.15	<10	<1	<0.02	<0.02	0.015

¹FA: Fly-ash, ²FBA: Furnace Bottom Ash, *Acidity hazard action value at 18 mol H⁺/t equivalent to pH 4.0

Table 4 demonstrates that only FA with pH at 4.0 or less had any requirement for liming capacity and these were associated with values of total oxidisable sulfur (%TOS).

DISCUSSION

The premise for undertaking an analysis of the CCPs using the methodology as developed for acid sulfate soils was to better identify properties of low pH ash. Current regulatory requirements are based on a standard pH determination at a 1:5 concentration of either soil or other material (NSW EPA 2010). In this study and comparison we identify that a low pH ash occurred when the standard pH value was below pH 4.0, and this corresponded to a measureable value of soluble acidity by the TAA test or as a net acidity value which includes the totalisation of soluble and oxidisable acidity (mol H⁺/t). We also identified that pH determinations of the TAA and the TSA solutions were consistent with a standard pH value being less than pH 7.

Consequently, we confirm that in this respect, there is validity in the quantitation of net acidity as derived for the ASS assessment to determine the potential for acidity risk. Of interest with the acidity determinations is that it is pH at pH 4 that will trigger measureable values of net acidity and a liming requirement. Consequently the premise of an environmental risk being defined by a pH value at less than pH 7.0 alone as a blanket regulatory policy, is not completely applicable to CCPs.

We identify that it was the fly ash and not the furnace bottom ash that had any measure of acidity and therefore the blanket determination for CCPs may only be relevant to fly ash. In practical terms the combination of a low pH ash at pH 4.0 had

less buffering capacity than the road base materials it was combined with. We show that in combination of fly ash with a pH 4 with an alkaline road base materials at pH 8.3 or above, would induce a slight pH reduction of 0.7 pH units, but only if the blended at 25%.

The data supports the previous observations that CCPs can have a low buffering capacity (Ward *et al.* 2009; Janowski *et al.* 2006) and we argue this can be quantified. Our results indicate all the CCPs tested had no residual sulfidic acidity, which is consistent with a highly oxidised material.

The buffering capacity of an acidic ash is a measure of the potential for the ash to produce acidic ions. In other words it indicates the extent to which an acidic material when mixed with a neutral material will continue to be acidic. Unlike Portland cement, low pH ashes do not have a high buffering capacity. As such when mixed with an alkaline road base material the pH of the overall mixture remained alkaline. Evident within this work is that addition rates of 25 % were needed to reduce the alkaline pH value but the initial response to the alkaline road bases and acid fly ash was a temporary increase of pH with blends at 10 % and at 25% where a pH reduction was developed. A response may be associated with the oxide compositions of the materials such as reactive calcium and or magnesium. Alternatively, pH of acid road base remained acidic irrespective of the blend percentages. Of interest is a future assessment of the amount of net acidity derived with these same road base blends, when compared to the fly ash as initially blended.

The SPOCAS assessment will determine the amount of pure CaCO_3 needed to neutralise the net acidity, and for these samples the acidity was identified within the soluble-exchangeable component, only if the fly ash was acidic at less than pH 4.0. This liming capacity is determined by the addition of results for Potential Sulfidic Acidity ($\text{mol H}^+/\text{t}$) + Actual Acidity ($\text{mol H}^+/\text{t}$). For the coal ashes tested, the calculated result for the most acidic fly ash, with a pH value ($_{1:5\text{dH}_2\text{O}}$) of 3.4 pH units was 2.18 kg CaCO_3/t to fully neutralise its acidity. When a factor of safety of 1.5 is included the liming capacity to neutralise the net acidity was 3.2 kg Ag Lime/t, or 3.2 g Ag Lime / kg of the acidic fly ash (Table 4). Therefore, because some fly ash below pH 5 may not have a significant lime requirement we suggest net acidity and liming capacity is included as a routine test for regulatory assessment of CCPs.

RISK ASSESSMENT

In this analysis of CCPs by the ASS and SPOCAS methodology, we quantify net acidity and therefore risk, submitting that this is a valid proposition with which to interpret risk with use of CCPs for land applications. For an ASS, the potential export of acid deemed as an environment risk is the sum of the capacity to create acid and the capacity to render acid ineffective, rather than neutralise (Mulvey 2004). Mulvey notes that S_{POS} , represents the maximum amount of acid which can be generated by reduced sulphides in the soil matrix when oxidised, which is the % H_2O_2 oxidisable S and total oxidisable S (TOS), if no buffering capacity was available and thus, the TOS and the net acid should have the same value. Within this context of ASS and their management, the risks are inherent within sulfidic soils. Applying this same assumption to CCPs in this study, we propose that risk of acidity potential to the surrounding environment when quantified by the S_{POS} values of the SPOCAS assessment confirms low risk or no risk, because all ashes except one of pH 9.5 had

any potential for oxidisable sulfidic acidity. We suggest that this SPOCAS calculation of sulfur-based acidity identifies the low risk of sulfidic acidity for coal ash materials generally, which is a correct representation for the oxidation process of coal combustion.

Acidity hazard is identified using net acidity values (Ahern *et al.* 1998) at the level of 18 mol H⁺/t. Consequently only fly ash would be considered a potential risk. Consequently the values as derived for TAA and net acidity with the corresponding calculation for liming would indicate if there is a potential for risk. The question is whether action values for acid sulfate soils at 18 mol H⁺/t are those that can be applied to CCPs as raw materials, or should be defined within the end use as the civil application.

We found that acidity associated with CCPs was as soluble/exchangeable acidity or soluble alkalinity, which is a consistent characteristic of the dominant alumina-silicate, iron silicate elemental structure of all coal ashes (Ward and French 2006). It is also a consistent factor of alkaline CCPs as assessed for civil applications (Sear *et al.* 2003). This is supported with the low values of S_{pos} and the high correlation between the sulfate and total elemental sulfur (r^2 9.447). In this case we propose that the TAA would be a suitable test to indicate acidity potential and that net acidity will indicate the need an active management option, given the action value already developed for ASS.

In summary, actual acidity is largely the readily soluble and exchangeable acidity, measured by titration of a 1 M KCl suspension. Retained acidity is stored in largely insoluble compounds such as jarosite and other iron and aluminium sulfate minerals, not measured by TAA titration (Ahern *et al.* 2004). Net acidity is a calculation assuming 1 mole of net acid soluble sulphur produces 3 moles of acidity. Net acidity (acidity) and net-acidity-sulfur units are retained forms of acidity. Net acidity is a value determined from sulfur values measured from the TSA. It is also used to calculate the amount of lime (CaCO₃) to counter act the net acidity when identifying the potential of remediating in situ soil net acidity within an ASS site.

For CCPs assessed in this study, those with a net acidity of above 15 mol H⁺/t and up to 42 mol H⁺/t, the liming capacity was 1.1 and 3.2 kg CaCO₃/t respectively. These values include the safety factor of 1.5. In practical terms this is about 2 kg CaCO₃/t. Given a daily production of say 2,500 tonnes of CCPs, there would be 5000 kg or 5 tonne lime requirement to neutralize acidity.

We acknowledge that this study represents a small sample size of the possible seventy two (72) coal ash types available for analysis across the ADAA membership. We propose that a model of acid-based accounting is a suitable suite for CCPs assessments and is an acceptable method for pH characterisation to identify (i) the need for acid neutralisation by lime or other alkaline material blending application and (ii) identify acidity hazard. However, to maximise the information gained using SPOCAS in this assessment, for completeness, further comparisons are needed that include the direct determination of chromium reducible sulfur rather than rely on the derived calculation of S_{POS}, because some values may be under-estimated when only using the SPOCAS methodology.

CONCLUSION

Our hypothesis was that the ASS methodology of analytical assessment by SPOCAS would be an informative model when applied to CCPs. By the SPOCAS analysis, with the acidity trail we identified that a low pH coal ash of less than pH 7 was not generally indicative of a net acidic risk unless below pH 4.0 and that a fly ash, not furnace bottom ash, may need neutralising.

We showed that an acidic fly ash did not significantly reduce or change the pH of an acidic or alkaline road-base material, and a 0.7 pH unit reduction was obtained when the original road base material was pH 9.4 and only if at a 25 % blend.

Low pH fly ashes when blended with alkaline aggregates produced a blend that remained alkaline. Where the low pH ash was blended with an acidic aggregate, the resultant material remained acidic.

Further investigations using the addition of lime to the acidic blends to determine whether an alkaline product could result are recommended. Also beneficial would be further investigations of ash pH influences to road base properties.

We conclude that regulatory limitation to CCPs where pH is less than 7 is overly conservative. If acidity is quantified then blending with slightly alkaline materials for use civil applications can mitigate the low pH nature of CCPs used.

The ASS methodology does provide an avenue for quantifying net acidity, and in this work we have shown the potential for using this type of quantitative approach. However further work is needed to fully develop the applicability of action values as derived for ASS. Such an assessment may also utilize general comparison using a standard acidity titration for H^+ used to determine agricultural soils.

REFERENCES

ADAA (2005) Guide to the use of Coal Combustion Products (Fly Ash and Furnace Bottom Ash) in roads and embankments. Ash Development Association of Australia, Wollongong, Australia. ISBN 0-9579274-1-X.

Ahern CR, Ahern M, Powell B (1998) Guidelines for sampling and analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998, Department of Natural Resources, Indooroopilly, Queensland, Australia.

Ahern CR, McElnea AE, Sullivan LA (2004) 'Acid Sulfate Soils Laboratory Methods Guidelines.' Queensland Department of Natural Resources, Mines and Energy: Indooroopilly.

Brownfield ME (2002) Characterization and modes of occurrence of elements in fired coal and fly ash – an integrated approach. United States Geological Survey Fact Sheet-038-02. 4 pp.

Jankowski J, Ward CR, French D, Groves S (2006) Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems. Fuel

86, 243-256.

Kutchko BG, Kim AG (2006) Fly ash characterization by SEM-EDS. *Fuel* 83, 2537-2544.

McElnea AE, Ahern CR, Menzies NW (2002) The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* 40, 301-309.

Mulvey P (2004) Acid Sulfate Soil: A review of methods, an interpretation of chemistry and derivation of hazard assessment. Technical Paper 17, Copyright 1999-2204 Environmental & Earth Sciences, Waverton NSW.

NSW EPA (2010) Protection of the Environment Operations (Waste) Regulation 2005 – General Exemption Under Part 6, Clause 51 & 51A: The coal ash exemption 2010. Office of Environment & Heritage, Sydney.

Rayment GE and Lyons DJ (2011) Acid Sulfate Soils Chapter 20, Soil Chemical Methods – Australasia. CSIRO Publishing, Collingwood, Victoria, Australia.

Roy WR, Griffin RA (1984) Illinois Basin coal fly ashes. 2: Equilibria relationships and qualitative modelling of ash-water reactions. *Environmental Science and Technology* 18, 739-742.

Sear LKA, Weatherley AJ, Dawson A (2003) The environmental impacts of using fly ash – The UK producers' perspective. Proceedings of International Ash Utilisation Symposium, Lexington, Kentucky. 14 pp.

<http://www.ukqaa.org.uk/Papers/KentuckyAshSymposiumLKASearEtAl2003.pdf>

Standards Australia (1996) AS1141.3.1 Methods for sampling and testing aggregates - Sampling – Aggregates. Standards Australia Limited, Sydney, NSW 2001, Australia.

Sullivan LA, Bush RT, McConchie D, Lancaster G, Clark M, Lin C and Saenger P (2004) Chromium reducible sulfur (Scr) – Method 22B. In 'Laboratory Methods Guidelines 2004-Acid Sulfate Soils. Queensland Acid Sulfate Soil Technical Manual'. (Eds CR Ahern, AE McElnea, LA Sullivan) (Department of Natural Resources and Mines: Indooroopilly)

Ward CR, French D (2006) Determination of glass content and estimation of glass composition in fly ash using quantitative X-ray diffractometry. *Fuel* 85, 2268-2277.

Ward CR, French D, Jankowski J, Dubikova Li Z, Riley KW (2009) Element mobility from fresh and long-stored acidic fly ashes associated with an Australian power station. *International Journal of Coal Geology* 80, 224-236.