THE GEOCHEMISTRY AND ECOTOXICOLOGY OF BAYER LIQUORS USING DIFFERENT NEUTRALISATION TECHNIQUES

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Abstract

Neutralisation of Bayer liquors provides a means of reducing the caustic nature and alkalinity of the red mud discharge so that muds maybe dewatered. However, how the liquor is neutralised provides different results and different residual geochemistry, which then results in liquors with different ecotoxicology. Five neutralisation techniques of Bayer liquor are investigated, and the geochemistry and ecotoxicology assessed. Results show that raw liquor (the do nothing approach) possesses not only a high basicity, and alkalinity, but has a very high ecotoxicological response, whereas seawater neutralised liquor, and a hybrid liquor (CO_2, followed by seawater additions) have significantly lower basicity and alkalinity, and is the liquor most tolerated by the two test species. LC_{50} values for the small, freshwater planktonic crustacean *Ceriodaphnia dubia* (*daphnia*) a standard ectoxicology test species, are recorded for raw liquor (0.5 mL/L) < carbon dioxide neutralized liquor (16 mL/L) ≤ acid neutralised liquor (26 mL/L) < seawater neutralised liquor (74 mL/L) ≤ hybrid neutralised liquor (98 mL/L). For *C. dubia*, toxicity is mostly through osmotic shock for seawater and hybrid materials. However, for the marine species *Paracalliope australis*, an amphipod crustacean and non-standard ectoxicology test species, an LC_{50} of 400-570 mL/L are recorded for seawater and hybrid discharges, because of the tolerance to the Electrical Conductivity (EC), and soluble salts in these Bayer treatment liquors.

1. Introduction

One of the greatest challenges facing the aluminium industry is the environmentally sound disposal of highly toxic bauxite refinery residues (BRR) produced during alumina extraction using the Bayer process [1, 2]. This process produces a soluble sodium-aluminate solution [$NaAl(OH)_4$] for alumina precipitation, and iron oxy-hydroxide-rich solid residue (BRR) for disposal [1, 3]. Current worldwide estimates of BRR production are well in excess of the 1998 estimates of 70 million tonnes annually, making BRR the world's highest volume industrial waste [3, 4].

The toxicity of BRR is potentially due to; high sodium content (> 50 g/kg); complex mineralogical make-up; fine particle size (> 90% is < 10µm), low plant nutrient concentrations, high soluble alkalinity (generally 30 g/kg as equivalent $CaCO_3$), and the pH of 11-13 [1, 2, 4-6]. The physical properties of BRR also make handling, transport and treatment difficult and regulatory control as a contaminated waste [3, 7] limit transport, storage, disposal, treatment applications, and reutilisation options. The high alkalinity of un-neutralised BRR destabilizes organic matter by oxidation, increases the solubility of metals, reduces solubility of plant nutrients and generates inhospitable conditions for plant growth [8].

Considerable research has been conducted to identify avenues for utilising the geochemical and physical characteristics of BRRs in ways that are ecologically and economically viable, as well as potentially beneficial [3]. The long-term neutralisation of BRR has resulted in successful reestablishment of flora and fauna in BRR impoundment areas, the removal of trace metals from contaminated areas and waste materials, and in the remediation of acid sulphate soils [1, 8-11]. Although there are several methods for neutralisation of BRR, this study investigates the acute toxicity of untreated supernatant liquor, and decant liquors of BRR neutralised using sulphuric acid, gaseous CO_2, seawater, and a hybrid neutralisation method involving both gaseous CO_2 and seawater.

1.1 Acid Neutralisation

The use of sulphuric acid to neutralize BRR is a way of rapidly lowering pH and reducing alkalinity. Al is precipitated in the form of gibbsite [$Al(OH)_3$], which requires a reduction of pH to < 8; equation 1[5].

$$H_2SO_4 + 2NaAl(OH)_4 \rightarrow Na_2SO_4 + 2Al(OH)_3 + 2H_2O \quad \textbf{1.}$$

1.2 Carbon Dioxide Neutralisation

There are several potential long-term environmental benefits of CO_2 neutralisation of BRR including carbon sequestering, and the opportunity for utilisation of the neutralised material [1, 2]. Cooling et al. [2] determines that CO_2 neutralisation is achieved by dawsonite precipitation (Equation 2) and that as much as 25 kg CO2/kL BRR slurry can be consumed; although Johnston et al [3] did not observe dawsonite precipitation, and suggest a simple alkalinity speciation conversion and gibbsite precipitation for CO_2 neutralisation (Equation 3).

$$[Al(OH)_4]^- + CO_2 + Na^+ \rightarrow NaAl(CO_3)(OH)_2 + H_2O \quad \textbf{2.}$$

$$2[Al(OH)_4]^- + CO_2 + 2Na^+ \rightarrow 2Al(OH)_3 + 2Na^+ + CO_3^{2-} + H_2O \quad \textbf{3.}$$

1.3 Seawater Neutralisation

The addition of seawater to BRR results in the reduction of salinity, sodicity and alkalinity, by converting readily soluble alkalinity into insoluble forms [1]. Mg primarily reacts with hydroxides, whereas the Ca more effectively reacts with soluble carbonates, although both Ca and Mg precipitate complex hydroxide-carbonates such as hydrotalcite, and Para-aluminohydrocalcite (Equations 4 and 5) [3, 5].

1.4 Hydrotalcite

$$6MgCl_2 + 2[Al(OH)_4]^- + 8OH^- + CO_3^{2-} + 12Na^+ \rightarrow Mg_6Al_2(CO_3)(OH)_{16}.4H_2O + 12NaCl \quad \textbf{4.}$$

Para-aluminohydrocalcite

$$CaCl_2 + 2[Al(OH)_4]^- + CO_3^{2-} + 2Na^+ \rightarrow CaAl_2(CO_3)_2(OH)_4.3H_2O + 4OH^- + 2NaCl \quad \textbf{5.}$$

1.5 Hybrid Neutralisation

Johnston et al. [3] suggests that low pressure CO_2 neutralisation precipitates minimal quantities of the soluble alkalinity thereby changing alkalinity speciation, but leaving total alkalinity relatively unchanged (Equation 3). Alkalinity precipitation, can then be achieved by seawater additions of Ca an Mg (Equation 6), giving a hybrid neutralisation [3].

$$2CO_3^{2-} + Ca^{2+} + Mg^{2+} \rightarrow CaCO_3 + MgCO_3 \qquad \textbf{6.}$$

1.6 Ecotoxicity Testing

Clearly refineries that wish to adopt a neutralisation process will produce a residual-liquor that will require discharge (usually to the environment), because unlike raw liquor it cannot be recycled back to the plant. However, the discharge practice will require appropriate permitting and through the approval process an understanding of the toxicity of the residual liquor will be required. Whole Effluent Toxicity Tests (WETT) [12] are used to, determine acceptable effluent dilution ratios, and cause-effect relationships between toxicants and aquatic ecosystems [13]. This toxicity testing approach presumes that the response of a small number of indicator species can estimate potential toxicities to other species [14]. Consequently, WETT tests allow a first-tier investigation of effluent toxicities, usually on a short term or acute basis. However, caution must be exercised in the interpretation and extrapolation of data from such laboratory-based toxicity tests, although the standardisation allows data to be used as a guide for sub-lethal, multi-species and field-based ecotoxicological investigations. WETT tests provide an important screening procedure that may then be taken to more comprehensive testing regimes [13-15].

Unfortunately, there are few toxicological studies of neutralised BRR liquors and here we provide a first toxicological screening of raw and neutralised supernatant liquors from BRR, utilising standardised 48-hour acute toxicity test protocols [18] with the standard freshwater invertebrate test species *Ceriodaphnia dubia*. Additional tests were conducted using a marine invertebrate species, *Paracalliope australis*, to provide an indication of the effects for a coastal discharge. Estimates of the LC_{50} (concentration to cause 50% of the test population) and LC_5 (concentration to cause 5% mortality of the test population) for *C. dubia* and *P. australis* after exposure have been made.

2. Methods

Raw Supernatant Liquor (RL) was extracted from an un-neutralised BRR that had become desiccated during storage by homogenizing with an equal volume of Milli-Q water. The slurry was left to settle for 24 hours before the liquor decanted and residual solids centrifuged at 3000 rpm for 10 minutes; 20 L were extracted. The extracted RL was then adjusted by an addition of 5 g/L Na_2CO_3, 5 g/L NaOH and 1g/L Al to bring alkalinity and Al concentration to values reported by McConchie et al. [16]; this RL became the stock for all testing and neutralisation regimes.

2.7 Neutralisation of RL

A 1.2 L sample of RL was neutralised using 20 mL of concentrated (18 M) Analar grade sulphuric acid to produce acid neutralised supernatant liquor (ANL). Acid was added in small 2 mL aliquots to the continuously stirred RL and allowed to react for several minutes before addition of the next aliquot of acid; a final pH of 8.2 was attained for the sample. A CO_2 neutralised supernatant liquor (CNL) was produced by taking a 1.5 L sample of RL and bubbling CO_2 gas through an aquarium stone at a rate of 2 L/min, for approximately 25 minutes until a pH of 7.9 was achieved. To produce seawater neutralised supernatant liquor (SNL) seawater was added to 500 mL of RL at a ratio of 20:1 and allowed to react and settle for 30 minutes; the resultant liquor was then decanted from the solids ready for use. The hybrid neutralised supernatant liquor (HNL), was produced by taking one litre of RL and introducing CO_2 via an aquarium diffuser stone at rate of 2 L/min until a pH of 9.97 was reached. The end pH of <10 is used as this is below the Basel Convention pH limit [7], and was achieved after 650 seconds of CO_2 addition. A 200 mL sub-sample of this CO2 treated liquor was removed, and added to 4 L seawater (20:1 dilution) to precipitate alkalinity.

2.8 Chemical Analysis of Supernatant Liquors

Three 50 mL replicate sub-samples of each of the five liquors and a seawater control were analysed for Na, Ca, Mg, Al and SO_4^{2-} concentrations, and electrical conductivity (EC) using standard APAH methodologies. In addition each liquor was titrated to determine total alkalinities using a Metrohm Titrando Auto titrator, and the titration data entered into the United States Geological Survey web-based alkalinity calculator [17] to determine alkalinity speciation.

2.9 Acute Toxicity Testing

USEPA test protocols for static, non-renewal 48-hour acute toxicity [12] were adhered to for all range finding and definitive tests. For *Ceriodaphnia dubia*, each test had five replicates, of five liquor concentrations for each neutralisation technique; for quality control of the test organisms. Liquor concentration ranges (Table 1) were defined by range finding tests, and definitive tests were repeated five times. Each replicate had five neonates (<24 hours old) with a total of 25 organisms for each concentration; four controls each containing 5 neonates were run concurrently.

Table 1: Concentrations of liquors for acute toxicity tests (shown as mL liquor/L dilution water, and as % liquor in solution).

No.	RL		ANL		CNL		SNL		HNL	
	mL/L	%	mL/L	%	mL/L	%	mL/L	%	mL/L	%
1	0.4	0.04	20	55	5.5	2	15	1.5	90	
2	0.45	0.045	25	70	7	2.5	16	1.6	100	10
3	0.5	0.05	27.5	80	8	2.75	17	1.7	105	10.5
4	0.55	0.055	30	90	9	3	18	1.8	108	10.8
5	0.6	0.06	35	100	10	3.5	19	1.9	110	11

However, because treated BRR liquors may be disposed of in marine systems [9], additional tests were also conducted using a marine invertebrate species *Paracalliope australis* [18], collected from Shaws Bay, Ballina, NSW, Australia, and identified at the Australian Museum. Two replicate tests were conducted using *P. australis* using the same protocols as for *C. dubia* [12]. Percentage mortality of test organisms in all treatments was recorded after 48 hours exposure in all tests and mean mortality calculated. Data was analysed using the Probit method [19] and concentrations predicted to cause mortality to an estimated 5% (LC_5), and 50% of the population (LC_{50}) are presented. Predicted dose-response curves for the neutralised liquors were also generated for C. dubia using predicted mortality concentrations of 1, 5, 10, 15, 50, 85, 90, 95 and 99% of the test population, using Probit.

3. Results

3.1 Chemical Analysis of Supernatant Liquors

Chemical analyses of liquors highlight considerable changes in the geochemistry of RL following all neutralisation techniques (Table 2). All techniques effectively reduced the high pH, Al concentration, hydroxide, and carbonate alkalinity in RL to potentially ecologically compatible levels. All neutralised liquors except CNL have greatly reduced total alkalinity (Table 2), which is consistent with the findings of Johnston et al. [3], where total alkalinity is essentially conserved, by conversion to bicarbonate alkalinity (Table 2); some Na reduction is observed suggesting

Dawsonite precipitates. In addition, all neutralisations resulted in liquors with increased SO_4^{2-} concentrations. RL has low SO_4^{2-} concentrations, as does CNL, however SNL and HNL have similar, but higher SO_4^{2-} concentrations (Table 2), which are very similar to the seawater used. Very high concentrations of SO_4^{2-} and Na concentrations were present in ANL, showing that the sulphuric acid had converted sodium hydroxides and carbonates to sulphates. Clearly all of the changes in anion concentrations and changes in cation composition affect electrical conductivity (EC). All neutralisations considerably reduced the high EC seen in RL primarily through a loss of hydroxide, which is particularly responsive to the probe. However the introduction of acid in ANL, and seawater in SNL and HNL, resulted in the higher EC seen in these liquors compared to CNL. Furthermore, neutralisation reduces Al concentrations, which were similar for CNL and HNL but more elevated for ANL; SNL materials have the lowest residual Al concentrations, which are primarily from the different neutralisation reactions taking place (Equations 1 to 5).

3.2 Ecotoxicological Analysis

Results from the initial range finding tests using *Ceriodaphnia dubia* were used to determine a suitable concentration ranges for liquors in definitive tests, which were; RL 0.4 to 0.6 mL/L; ANL 20 to 35 mL/L; CNL 15 to 19 mL/L, SNL 55 to 100 mL/L and HNL 9 to 110 mL/L (Table 1). Consequently, mean mortality data from five definitive test replicates using *C. dubia* provide LC_{50} (Table 3). This table (Table 3) also shows the estimates LC_5 and LC_{50} values for both species, and Figure 1 shows the predicted dose-responses curves for *C. dubia* using estimations of concentrations predicted to be lethal to 1, 5, 10, 15, 50, 85, 90, 95 and 99% of the test population (LC_{1-99}). All test data used in analyses had < 10% mortality in controls, and was analysed using the Probit method [25]. Figure 2 shows the predicted dose-responses curves for *Paracalliope australis showing a clear grouping of the treatment techniques*.

Table 2: Mean EC, Na, Ca, Mg, SO_4^{2-} and Al concentrations, and pH and total and alkalinity species (± standard deviations) in raw and neutralised liquor samples and seawater. Dark grey fill indicates orders of magnitude difference for analytes whereas lighter grey shades indicate other potential sources of toxicity difference.

Parameter	RL	ANL	CNL	SNL	HNL	Seawater
EC dS/m	77.1 (±3.1)	44.9 (±0.30)	36.0 (±0.1)	49.00 (±0.3)	49.1 (±0.1)	34.1 (±0.3)
Na (mg/L)	15900 (±1000)	17600 (±2300)	14200 (±250)	11300 (±280)	10900 (±430)	11000 (±330)
Ca (mg/L)	3.70 (±0.5)	0.57 (±0.7)	0.37 (±0.3)	336 (±2)	184 (±17)	398 (±6)
Mg (mg/L)	0.47 (±0.6)	0.33 (±0.2)	0.27 (±0.3)	910 (±30)	1160 (±50)	1360 (±60)
SO_4^{2-} (mg/L)	281 (±55)	34800 (±5000)	649 (±70)	3080 (±310)	3100 (±200)	3240 (±26)
Al (mg/L)	3820 (±180)	2.66 (±0.8)	0.77 (±0.02)	0.04 (±0.01)	0.56 (±0.02)	0.34 (±0.45)
pH	12.9 (±0.1)	8.2 (±0.1)	7.9 (±0.1)	8.7 (±0.1)	8.1 (±0.1)	8.3 (±0.1)
Total Alkalinity $CaCO_3$ (mg/L)	35600 (±4230)	5340 (±6)	30200 (±290)	361 (±35)	1390 (±130)	123 (±33)
Hydroxide OH^- (mg/L)	1040 (±190)	0.03 (±0.06)	<0.01	0.1 (±0.05)	0.1 (±0.05)	<0.01
Carbonate CO_3^{2-} (mg/L)	19700 (±2400)	101 (±4.1)	301 (±25)	10.4 (±5.4)	49.7 (±1.3)	0.43 (±0.15)
Bicarbonate HCO_3^- (mg/L)	59.8 (±10)	6310 (±5.4)	36200 (±400)	419 (±150)	1590 (±40)	149 (±40)

Table 3: Mean concentrations (mL/L) of liquors predicted to cause mortality to 5% (LC_5) and 50% (LC_{50}) at a 95% confidence interval, for test populations of *C. dubia* and *P. australis* in 48 hours exposure, calculated using the Probit method.

	RL (Raw Liquor) mL/L		ANL (Acid-neutralised) mL/L		CNL (CO_2-neutralised) mL/L		SNL (Seawater-neutralise) mL/L		HNL (Hybrid-neutralise) mL/L	
	C. dubia	P. australis	C. dubia	P. australis	C. dubia	P. australis	C. dubia	P. australis	C. dubia	P. australis
LC_{50}	0.42 (±0.07)	0.21 (±0.09)	25.0 (±3)	8.04 (*)	16.2 (±0.7)	6.68 (*)	73.9 (±5.7)	553 (±108)	97.0 (±3.9)	360 (±137)
LC_5	0.34 (±0.07)	0.03 (±0.02)	18.4 (±3.2)	2.45 (*)	13.0 (±1.7)	2.61 (*)	50.3 (±12)	286 (±122	81.8 (±8.4)	209 (±150

* upper and lower limits at 95% confidence not calculable for only 2 replicates

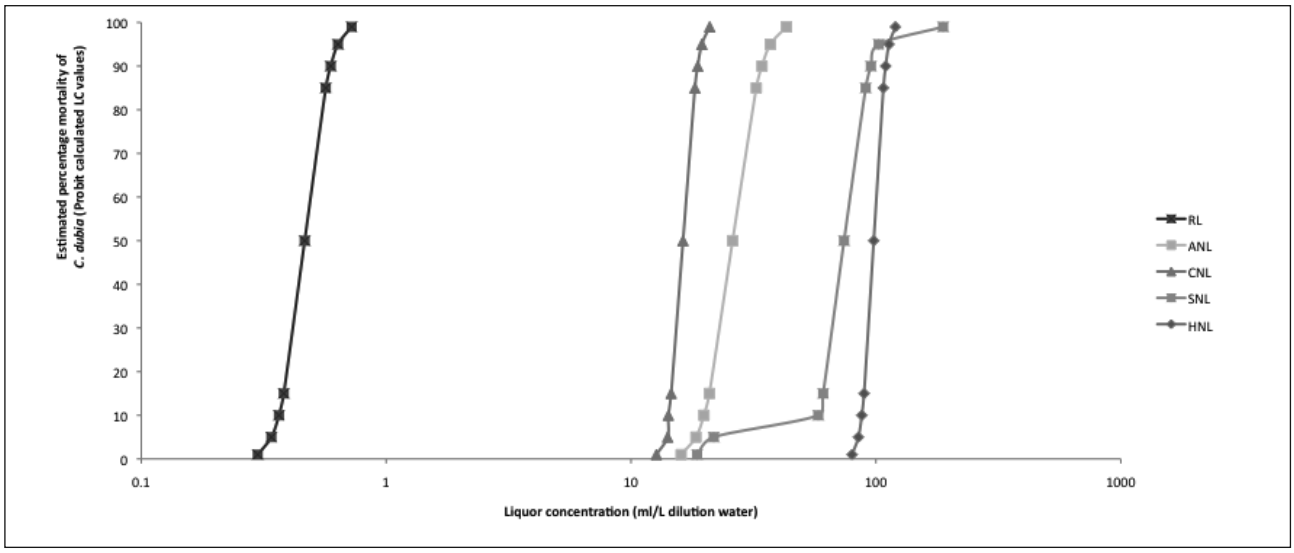

Figure 1: **Predicted 48-hour dose-response curves (mL/L) for *C. dubia*, calculated using the Probit method.**

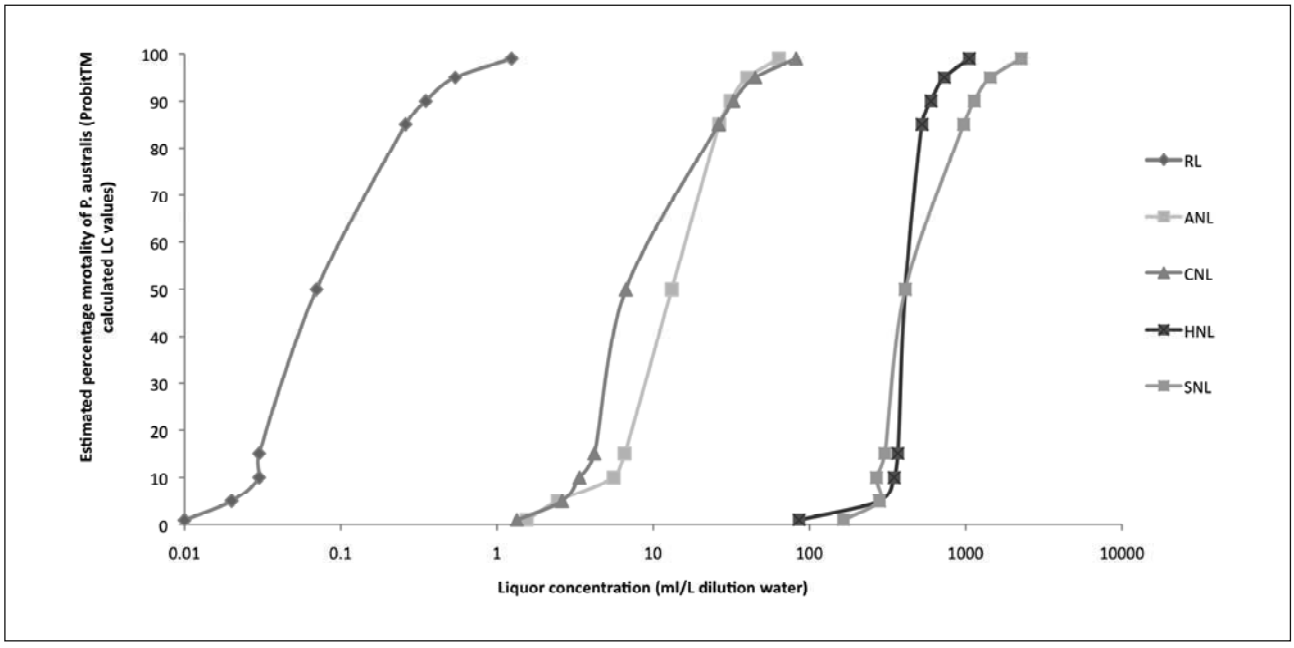

Figure 2: **Predicted 48-hour dose-response curves (mL/L) for *P. australis*, calculated using the Probit method.**

4. Discussion

This research provides new information on the acute toxicity of raw and four neutralised supernatant liquors from BRR, and provides necessary baselines and information that may help identify potential directions for further ecotoxicological research of BRR materials. Moreover, the standard 48-hour acute toxicity tests using the standard freshwater species *Ceriodaphnia dubia*, and a marine amphipod *Paracalliope australis*, do show the relative acute toxicity of five supernatant liquors to these test species. *C. dubia* is a common heavy algal grazer considered representative of common zooplankton communities [20, 21] and is considered comparable to Daphnia magna, a species commonly used in ecotoxicology. *P. australis* is microphagous, both grazing on algae and filter feeding. Previous ecotoxicological studies have been done using this species as an indicator for macroinvertebrate communities, and was found by Hyne et al. [22] to be highly sensitive, and hence a potentially useful species for ecotoxicological investigations in marine environments.

4.1 pH

The high pH of BRR is considered to be the primary concern in regard to potential ecological impacts [1, 2, 4, 5]. Interpretation of chemical analyses and ecotoxicological test results in the present study suggest that toxicity of RL to *Ceriodaphnia dubia* and *Paracalliope australis* is primarily due to the high pH (12.9) and high total and hydroxide alkalinity. *C. dubia* has previously been found to be sensitive to changes in alkalinity and pH, with significant impairment of survival and reproduction with a pH outside the range of 6.14 – 8.99 [23]. However, recent from Howe et al. (Accepted) suggests that *C. dubia* is quite tolerant of pH's up to 9.5, however it is known that the acute toxicity and behaviour of some trace-metals is affected by changes in pH [20, 21]. Brunori et al. [1] suggests that reductions in pH in seawater neutralisation of BRR deem it ecologically safe, hence the reduced pH of neutralised liquors appears most influential in reducing test organisms toxicity.

4.2 Alkalinity

Alkalinity variations causes fundamental change in ecosystems, and the toxicity of effluents is often primarily due to high alkalinities [21]. High total, hydroxide, and carbonate alkalinity in RL are likely to be the main causes of mortality in this liquor, along with pH (Table 2 & 3). The concentration of these alkalinity species is seen in this study to have direct correlations with relative toxicity of liquors. Total alkalinity is near completely removed in 3 of the 4-neutralisation methods (Table 2; Figs. 1 & 2); CNL retains the high total alkalinity of RL. However, CNL changes the alkalinity speciation with increased bicarbonate alkalinity, and is more toxic than liquors with a similar pH, but lower total, and bicarbonate alkalinities. Neutralisation with acid saw a great reduction in total and carbonate alkalinity (Table 2) and a near-complete removal of hydroxide alkalinity, as also seen in other neutralised liquors (Table 2). ANL had elevated bicarbonate alkalinity concentrations compared to SNL and HNL (Table 2), apparently contributing to the higher toxicity. It would appear that the conversion of soluble alkalinity to low-solubility minerals (e.g. Ca, Mg, carbonates, hydroxides and hydroxy-carbonates) in both SNL and HNL reduces one of the most toxic characteristic of BRR (alkalinity) [1].

4.3 Electrical Conductivity (EC), Na, Ca, Mg and SO_4^{2-}

The high EC seen in BRR is due mostly to Na, OH-, and in the case of ANL, $SO_4$2- concentrations (Table 2) [6]. RL has a much higher EC than other liquors, and the neutralisation of BRR using any of the described techniques reduces the EC to potentially ecologically sound levels. In alkaline conditions, high Na concentrations may impair physiological functions, and tends to result in poor structural characteristics of solids, causing BRR impoundment sites to readily eroded, have a tendency to crack, swell, and form a surface crust not conducive to re-vegetation [6]. Additionally, Kennedy et al.[20]29] suggests that the acute and chronic toxicity of a coal-mine waters is mostly from Na, concentrations of which in BRR are >5 times the concentration reported by Kennedy et al [20,29].

Chemical analysis shows the Na concentration in liquors was reduced when RL is neutralised with seawater or the hybrid method (Table 2) mostly by dilution. The Na concentration increased in ANL and remained relatively unchanged when liquor was neutralised with CO_2 alone in CNL (14200 ± 252 mg/L). Lower concentrations of Na in both CO_2 neutralised liquors (CNL and HNL), suggests that there is a precipitation of dawsonite, which is consistent with Cooling et al.[2]. However, Johnston et al.[3] found no dawsonite precipitation, perhaps due to lower Al concentrations in their liquors, than those present in liquors used in this study (~ 500 mg/L [3], compared to a mean of 3821 mg/L in the RL here).

RL, ANL and CNL had relatively low concentrations of calcium and magnesium (Table 2). High concentrations of Ca and Mg in SNL and HNL may explain the differences in mortality of test species between the freshwater *Ceriodaphnia dubia* and the marine *Paracalliope australis* in these liquors. As previously discussed, tests with RL, ANL and CNL induced similar responses from these two species, with the LC_{50} differing by no more than 10 mL/L between species. SNL and HNL were three and seven times less toxic, respectively, to *P. australis* than to *C. dubia*. As seen in Figures 1 & 2 and Table 2, and high mortality of *P. australis* did not occur except in relatively high concentrations of SNL and HNL. Both these liquors caused mortality to less than 20% of this species at liquor concentrations over 35% (LC_{50} values of 567.36 ml/L SNL and 379.045 mL/L HNL). In the context of the similar responses of these species to other liquors, the high concentrations of Ca and Mg in SNL and HNL are likely to have caused mortalities to *C. dubia* due to osmotic shock, and not because of toxicities directly associated with BRR.

High concentrations of Ca and Mg (particularly Ca), can potentially compete with, and reduce the toxicity of trace metals in aquatic systems [13] and alleviate the toxic effects of Na [20]. This is reflected in results of chemical and toxicity data here, where SNL and HNL were considerably less toxic to both test species than other liquors, with LC_{50} values up to 1000 times that of RL. The addition of seawater also reduces the sodium adsorption ratio (SAR), improving soil characteristics and promoting revegetation of BRR impoundment areas [6]. The addition of sulphuric acid to the system during neutralisation with acid resulted in the high SO_4^{2-} concentration in ANL (34806 ± 5000 mg/L), 34 times the concentrations found by Soucek [24] to cause impairment of long-term reproduction success of *Ceriodaphnia dubia*. Kennedy et al. [20] also found *C. dubia* to show high sensitivity to SO_4^{2-}, and determined SO_4^{2-} (at concentrations of ~ 2000 mg/L) to be a primary source of acute and chronic toxicity of a coal mine effluent to this species. The results of ecotoxicological tests in this study suggest that high concentrations of dissolved SO_4^{2-} contributed to the toxicity of ANL to both test species, and that SO_4^{2-} in combination with Na, Ca and Mg in both SNL and HNL was a cause of lethality, inducing osmotic shock in the freshwater *C. dubia*.

4.4 Aluminium and other trace-metals

RL samples had mean Al concentrations of 3820 ± 182 mg/L, which is considered to be a primary source of toxicity in this liquor, with high pH and alkalinity. All neutralisation techniques resulted in the precipitation of Al (Table 1). Studies have indicated that Al concentrations hinder plant growth in BRR, e.g. [5], and the potential toxicity of Al to all flora and fauna, particularly aquatic species, is widely known. However, high alkalinity and Ca concentrations are known to act antagonistically, potentially reducing toxic effects of metal toxicity in aquatic systems [25].

The high Al concentration in ANL (Table 2) is due to the precipitation of gibbsite that occurs with the addition of acid. This reaction requires a lower pH than other neutralisation methods (equation 2) as discussed by Sturt [5]. The pH of 8.2 in CNL is described by Sturt [5] to be near the threshold (~ pH 8) for inducing Al precipitation to concentrations in solution below 3 mg/L, and because of this ANL had the highest Al concentrations of all neutralised liquors (2.66 ± 0.82 mg/L) which may have contributed to toxicity. The bioavailability of trace metals is dependent on chemical conditions in a water body [25]. Soucek et al. [26] found that in acid mine drainage, Al and Fe may be a primary causes of acute toxicity to C. dubia when these metals are in transition from acidic conditions into pH neutral water bodies, and reported that diversity in benthic macro-invertebrates communities was considerably impaired in pH neutral waters more than 1 km from a site of acidification. This may have ecotoxicological ramifications for the application of neutralised BRR materials in acid environments.

The most sensitive life stages to trace-metals are generally considered to be embryonic and larval stages though there are other parameters to which older life stages may be more susceptible [23]. The use of *Ceriodaphnia dubia* neonates (< 24 hours old) in this study provides necessary baseline data. However, the next tier of ecotoxicological investigations should involve a series of sub-lethal tests on an array of species and life stages relevant to specific areas of liquor discharge, and with consideration of the various pathways of uptake of trace metals [13, 14, 27]. His et al. [28] found that it was the sediment bound metal species present in BRR that were the most bio-available and toxicologically important. Hence, the potential toxicity of the trace-metal component of BRR in this study may be underestimated, as test organisms were not exposed to the sediment-bound fraction of heavy metals. Also, acute toxicity test

protocol requires that test organisms are unfed during tests [12], and therefore are not exposed to dietary uptake of heavy metals, but only to heavy metals in the water column. Therefore, sediment toxicity tests and investigations into acute and chronic effects of dietary uptake of heavy metals from BRR materials are necessary.

4.5 Summary of primary toxicities

Interpretation of chemical analysis and ecotoxicological tests in this study provides indication of the likely primary causes of acute toxicity (for each liquor) to each test species (Table 4). This new information may help in guiding further efforts to alleviate the toxicity of BRR materials and enable their beneficial utilization.

4.6 Relevance of laboratory toxicity tests

Laboratory acute toxicity testing is an essential starting point for ANZECC decision-making tree regarding ecological risk assessment, and providing for subsequent toxicological tests [29, 30]. Moreover, these tests provide important for initial observation of test organism response to a contaminant with the necessary elimination of environmental variables. Consequently, results must not be viewed, interpreted, or extrapolated on, out of context [30-32]. Moreover, there is evidence that responses in seven day reproduction tests with *Ceriodaphnia dubia* do not necessarily provide a valid indication of effects on full life cycle reproduction [15, 33], as unnatural food concentrations during laboratory culturing may have significant impact on responses to toxins [23], and that intermittent exposure to toxins is often more detrimental to ecosystems than consistently lower, or average concentrations [31]. Hence, these issues require the integration of ecologically minded thinking and observation, in combination with controlled ecotoxicological investigations.

Table 4: Suggested primary causes of acute toxicity in each of the liquors to test species (Concentrations of liquors in mL/L DW).

Liquor type	Primary Source(s) of Toxicity	
	Ceriodaphnia dubia	***Paracalliope australis***
RL	pH and alkalinity (primarily hydroxide)	pH and alkalinity (primarily hydroxide)
ANL	Total dissolved salts (Na and SO_4^{2-}), EC, and Al	Total dissolved salts (Na and SO_4^{2-}), EC, and Al
CNL	Total and alkalinity (primarily bicarbonate)	Total dissolved salts (Na^-), and alkalinity (primarily bicarbonate)
HNL	Osmotic shock due to high salt concentration and EC	EC, high SO_4^{2-} and alkalinity. Slightly more toxic than SNL perhaps due to a lower Ca:Mg ratio and higher Al concentration
SNL	Osmotic shock due to high salt concentration and EC	EC, SO_4^{2-}, alkalinity

5. Conclusions and Recommendations

This research provides data on the acute toxicity of raw supernatant BRR liquor (RL), and liquors neutralised using acid (ANL), CO_2 (CNL), seawater (SNL), and CO_2 followed by seawater (hybrid method; HNL). Analysis of mortality data found the estimated LC50 values for *Ceriodaphnia dubia* to be; RL (0.5 mL/L) < ANL (16 mL/L) ≤ CNL (26 mL/L) < SNL (74 mL/L) ≤ HNL (98 mL/L). Additional tests using the marine species, *Paracalliope australis* show that although the toxicity of the liquors have a similar order, *P. australis* tolerates much higher concentrations of both SNL and HNL than *C. dubia*. Consequently, because it is a freshwater species, mortality of *C. dubia* in SNL and HNL was most likely from osmotic shock, suggesting these liquors may be tolerated by marine ecosystems much better and at higher concentrations than freshwater ecosystems. However, Figures 1 and 2 clearly show that for marine species treatments utilising seawater to precipitate are far superior in reducing environmental impact, particularly to marine species.

High pH, total alkalinity, and Al concentration are considered to be the primary causes of toxicity in RL for both the freshwater *Ceriodaphnia dubia* and the marine *Paracalliope australis*. High total alkalinity was also present in CNL, and although CNL and ANL were similarly toxic, the carbonation of raw liquor did not substantially reduce the total alkalinity and CNL is more acutely toxic to both species than ANL. Although, acid neutralisation effectively removes hydroxide alkalinity, and reduces total and carbonate alkalinity, high SO_4^{2-} and Na and Al concentrations in ANL are likely causes of toxicity.

The data obtained here provides new information on the ecotoxicology of BRR liquors and provides guidance for further ecotoxicological testing of BRR materials. Research into the effects of short-term pulses of effluents, and the potential behaviour of BRR materials under different chemical conditions are needed. These should involve neutralised BRR supernatant liquors and sediments on acute and chronic survival, reproduction, growth and behavioural responses of regionally relevant species in different life stages. The utilisation of more sensitive standardised laboratory based test types will guide the design of site-specific field-based tests, assessments and monitoring regimes.

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