GEOCHEMISTRY OF BAUXITE REFINERY RESIDUES NEUTRALISED BY DIFFERENT METHODS

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Abstract

Red mud remains the single biggest environmental problem for the alumina industry, because of the fine-grained nature (> 90% is < 10 μm), high pH (>13), high sodium concentration (>50 g/Kg), and high alkalinity (typically ≈ 30 g/kg as equivalent $CaCO_3$). However, neutralisation of red mud provides potential re-use options as a valuable resource and this paper investigates the geochemistry of 4 types of red mud: un-neutralised raw red mud (UNRM), a CO_2-neutralised red mud (CNRM), a Basecon™-neutralised red mud (Basecon™), and a CO_2-neutralisation followed by a Basecon™-neutralisation (Hybrid) material. Investigations show that although the metal binding capacity for all samples was similar, the neutralisation techniques form two distinct geochemical groups: UNRM and CNRM, and the Basecon™ and Hybrid material. The UNRM and the CNRM have similar total alkalinities and phosphate loading capacities (<25 % removal). However, the alkaline species remain almost entirely soluble and convert from the hydroxide-carbonate dominated UNRM to bicarbonate-carbonate dominated for CNRM; pH falls from 13.2 to 7.5 for CNRM. The Basecon™ and Hybrid materials have similar total and speciated alkalinities (≈ 0.25g/L as equivalent $CaCO_3$) in the residual liquors. Solution pH, E.C. are similar to the CNRM material, whereas although phosphate-loading capacity for Basecon™ and Hybrid materials are similar to each other (>98 % removal), they are substantially greater than those for either the UNRM or CNRM. Hybrid material at this stage of our investigations appears to provide some environmental advantage to Basecon™ because of an additional ≈17 g/kg CO_2 consumption during the alkalinity transformation.

1. Introduction

1.1 Background

The alumina extraction process uses bauxite, found naturally as red-brown nodules containing gibbsite ($Al(OH)_3.3H_2O$), diaspore (β-AlOOH), boehmite (γ-AlOOH), and hematite (Fe_2O_3), which are digested in a caustic liquor (pH >12) of Na and Ca-hydroxides. This then produces two output streams, a liquor pregnant with alumina that is for alumina precipitation and a solid residue (Red Mud) for disposal. This waste residue is initially a slurry with a moisture content ranging from 50-70%, containing liquor, which is often re-cycled through the plant after filtration [1-3].

About 70 million tonnes of red mud is produced globally each year [4; 5] at a rate of 1.1 to 6.2 tons produced per tonne of alumina. Because of the high caustic content and sodicity, the wide range of trace metal contaminants, high pH (>13) and the alkalinity (>20,000mg/L as equivalent $CaCO_3$), red mud, therefore, represents a major ecological and economical problem worldwide [3; 4; 6-10]. Considerable research has been conducted on red muds, and although many efforts have been made to reduce or reuse this waste material the vast majority continues to go to surface impoundments for long-term storage. The geochemistry of red mud has it listed as a contaminated waste under the Basel Convention [11; 12], limiting its transportation for storage, disposal, or treatment applications and re-use options [3; 4; 7- 9; 13-16].
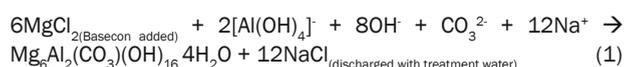
Because of the high acid neutralising capacity (up to 10 moles H^+/Kg, mainly via OH^- and CO_3^{2-}), and ability to bind many cationic and anionic ions, red mud and its derivatives have been used to treat acid mine drainage (AMD), acidic sediments and soils, and industrial effluents. In addition, red mud and its derivatives have successfully been used as a landfill cover, odour reducers, catalysts, road base, fertilizer filler, permeable reactive barriers, clay capping, ceramics, glass-ceramics, geopolymers, construction materials and synthetic soils [9; 14; 15; 17- 26].
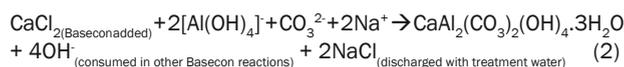
1.2 Current Treatment Techniques

Although many technologies researched to date are capable of reducing the volume of waste mud and producing useable products, three main neutralisations have the greatest potential to provide sustainable outcomes. These three methods are CO_2 gas re-circulation (Alcoa), Seawater neutralisation (QAL), and Basecon™ neutralisation (Virotec). Each method produces a final product with improved storage, transport and re-use options over raw red mud [14; 27- 29].

Seawater neutralisation of red mud involves the addition of excess seawater (up to 20 times the volume of mud) to precipitate the soluble hydroxides and carbonates as insoluble hydroxides ($Mg_3(OH)_6$), carbonates ($CaCO_3$ and $MgCO_3$) and hydroxy-carbonates ($Mg_6Al_2(CO_3)(OH)_{16}.4H_2O$, $CaAl_2(CO_3)_2(OH)_4.3H_2O$). The residual seawater then discharges back into the ocean after use [29; 30]. Red mud neutralised via the Basecon™ procedure [31] is Bauxsol™, and because Basecon™ is regarded as a manufacturing process, and is classified as environmentally non-hazardous [32, 33]. The Basecon™ procedure is similar to seawater neutralisation and uses artificial Ca and Mg-rich brines >20 times the concentration of seawater, where the Ca: Mg ratios can be varied to favour particular mineral precipitates [4; 13; 14; 15; 31]. The key chemistry of both Basecon™ and seawater neutralisation are the precipitation of hydrotalcite and para-aluminohydrocalcite (Equations 1 & 2), although other minor reactions of simple carbonates and hydroxides are also possible.

Hydrotalcite

$$6MgCl_{2(Basecon\ added)} + 2[Al(OH)_4]^- + 8OH^- + CO_3^{2-} + 12Na^+ \rightarrow Mg_6Al_2(CO_3)(OH)_{16}.4H_2O + 12NaCl_{(discharged\ with\ treatment\ water)} \quad (1)$$

Para-aluminohydrocalcite

$$CaCl_{2(Basecon\ added)} + 2[Al(OH)_4]^- + CO_3^{2-} + 2Na^+ \rightarrow CaAl_2(CO_3)_2(OH)_4.3H_2O + 4OH^-_{(consumed\ in\ other\ Basecon\ reactions)} + 2NaCl_{(discharged\ with\ treatment\ water)} \quad (2)$$

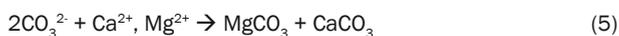CO_2 neutralisation utilises the reversibility of key alkalinity reactions between hydroxide, carbonate and bicarbonate. In addition, the consumption of CO_2 to reduce atmospheric and industrial carbon dioxide emissions via this sequestration technique could provide additional benefits. The conversion of the hydroxide (OH^-) component of the red mud to bi-carbonate, lowers pH to <8.5 and consumes CO_2. Soluble carbonate (CO_3^{2-}) and bi-carbonate (HCO_3^-) ions are then dominant products of the neutralisation process, adding to the alkalinity of the mud, although the precipitation of Dawsonite has also been observed [15; 27; 35]. The key chemistry of CO_2 neutralisation is:

$$[Al(OH)_4]^- + CO_2 + Na^+ \rightarrow Al(OH)_3 + Na^+ + HCO_3^- \tag{3}$$
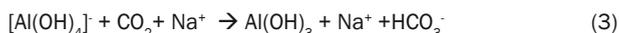
However, because the CO_2 method mostly affects the speciation of the alkalinity rather than solubility, there is further potential to combine CO_2 neutralisations with a Basecon™ neutralisation. The resulting chemistry does not provide the complex mineral precipitation of Basecon™ where the key chemistry should be:

$$2[Al(OH)_4]^- + CO_2 + 2Na^+ \rightarrow 2Al(OH)_3 + Na^+ + CO_3^{2-} + H_2O \tag{4}$$

$$2CO_3^{2-} + Ca^{2+}, Mg^{2+} \rightarrow MgCO_3 + CaCO_3 \tag{5}$$

However, a composite neutralisation has not been made previously, nor has the geochemistry of the solids been investigated previously. Because, each neutralisation technique has profound effects on the chemistry of the residual solids and the liquor in which neutralisation occurs, this paper compares these changes between un-neutralised red mud (UNRM), Basecon™, CO_2-neutralised red mud (CNRM), and CO_2-Basecon™-neutralised red mud (Hybrid), and how these changes affect potential environmental applications.

2. Methods

2.1 Sample Origin and Preparation

The raw red mud sample used throughout the experimental process originated from an Australian plant. The mud was thoroughly homogenised and a sub-sample was oven-dried at 65°C for 1 week then allowed to cool to provide moisture content. Solids required a 1:5 sample: reagent grade water extraction from the fresh red mud (tumble-mixed for 1 hour at 15 rpm before centrifugation at 3000 rpm for 10 minutes). The centrifuged supernatant liquor (SNL) was decanted filtered through 0.45 μm cellulose acetate filters and reserved. Samples treated by additional means, (eg CO_2, Basecon™ and the Hybrid method) are made using a known weight of fresh wet mud. After treatment, excess supernatant liquor is decanted and retained from centrifuged solids (3000 rpm for 10 minutes).

Solids were dried and crushed in the same manner as a red mud sample. All neutralisations used an initial solid/reagent water ratio of 1:5 (300g equivalent dry material: 1500mL) to create a slurry suitable for dissolution of soluble alkaline components, and to reduce sample viscosity to allow CO_2 gas to diffuse through as per the method detailed by Jones *et al.* [36]. A slight modification to Jones *et al.* [36] made here is a CO_2 bleed for 25 minutes not 20 minutes. Table 1 summarises the neutralisation steps used for each neutralisation technique; replicate testing of samples in triplicate produces statistically valid data.

Table 1. Neutralisation procedure used for the four samples tested

Parameter	UNRM	CNRM	Basecon™	Hybrid
Initial mix time (min)	30	30	30	30
CO_2 addition	na	200 mL/min for 25 min	na	200 mL/min for 25 min
$CaCl_2.2H_2O$ addition	na	na	21.74g	21.74g
$MgCl_2.6H_2O$ addition	na	na	132.42g	132.42g
Final mix time (min)	30	30	30	30
Settling	Overnight	Overnight	Overnight	Overnight
SNL Filtration	0.45 um paper	0.45 um paper	0.45 um paper	0.45 um paper

2.2 Analytical Methods

SNL from a 1:5 solid: reagent water 1hr extraction for pH and electro-conductivity (E.C.) analysis are determined with probes calibrated to a slope of >98% and an asymmetry of <0.1 using pH 4 and 7 buffer solutions. The E.C. of solutions was determined with probes calibrated to K= 1.00 (+/- 0.05) in a 2.76 mS/cm solution. SNL alkalinity uses a 30 mL sub-sample of unfiltered raw or neutralisation liquor, which is titrated against 0.1 N HCl. Acid, pH, E.C., temperature and titration data (millilitres added and pH) entered into USGS Web-based Alkalinity Calculator (http://or.water.usgs.gov/alk/). Alkalinity and speciation are calculated using Fixed-endpoint method for reporting; samples are filtered at pH 7.5 to remove the precipitates that form.

The acid neutralisation capacity (ANC) test determines the total concentration of H^+ that can be neutralised or sequestered into the solids at pH 4.5. 15 g of sample was added to 40 mL reagent-grade water to allow constant stirring; the slurry is then titrated against 0.1 N HCl. Acid, pH, E.C., temperature and titration data are entered into USGS Web-based Alkalinity Calculator (http://or.water.usgs.gov/alk/), and calculated using the Fixed-endpoint method for reporting.

2.3 Metal and Phosphate Binding

The metal loading test assists in quantifying the capacity of the solids to bind a metals from a mixed metal solution. A 5 g sub-sample is added to 50 mL of a Synthetic AMD solution (made from analytical standards acidified to pH 2.5 with 1 M sulphuric acid). Samples are tumbled for 24 hrs at 15 rpm, centrifuged for 10 min @ 3000 rpm and the decanted SNL filtered (0.45 μm cellulose-acetate membrane) and analysed for Total metals by ICP-MS and ICP-OES analysis. The residual solids are dried overnight at 65°C for 24 hrs, and crushed in a ceramic mortar and pestle. A 2 g sub-sample of these residuals was then TCLP extracted and analysed for leachable metals [37; 38], using ICP-MS and ICP-OES.

The phosphate-loading test is used to quantify the capacity of the solids to bind phosphate from solution by using 10g of solid to 50 mL PO_4 solution. Each sample was tumble-mixed for 24 hours @ 15 rpm, centrifuged for 10 min @ 3000 rpm before decanting 30 mL for phosphate (total P) analysis using the standard molybdenum-blue method [37].

All samples for analysis were submitted to a NATA registered laboratory, with at least 10% of all samples being either duplicate analyses, known analytical standards, blanks, and spiked samples, for QA/QC. Duplicate samples provided an agreement of >98%, and analytical standards were ± 2% of stated concentrations; whereas spike additions indicate the 97-102% recovery of the spike; and blanks yielded analyses of <5 times detection limits. These QA/QC data indicate that the analyses of waters and extracts are reliable indicators of the concentrations expressed.

2.4 Solids Bulk Chemistry

Crushed samples of each solid mounted on aluminium stubs and carbon coated for visual and EDAX (Energy Dispersive Analytical X-Ray) analysis. Analyses are made using a Cambridge SEM, and the EDAX analyses performed using an Oxford EDAX attachment. EDAX elemental responses are calibrated using multiple standards, on Wollastonite, Aluminium, Pyrite Titanium, and Iron. Spot EDAX analysis are conducted on 15 sample locations for 300 seconds at 20 kV and 2.7 mA to collect elemental data, for each sample for indicative purposes on the mineral composition of the solid; some 200 spot analyses would be required for statistical validation, on random spots [39].

3. Results & Discussion

3.1 Alkalinity, pH and Electro-conductivity

Table 2 summarises the pH, E.C., total and speciated alkalinity data for the sample SNL's and solids. The data shows distinct changes in the pH and E.C. between the UNRM SNL and the three neutralised SNL's. The application of a neutralisation technique to un-neutralised red mud resulted in a substantial fall in the pH of the system. However, such changes in the total alkalinity of the SNL are not observed for all the neutralisation techniques, for example, there is no substantial change in the total alkalinity from the UNRM by the CO_2 neutralisation. Whereas, the Basecon™ and Hybrid neutralisation methods show a substantial reduction in SNL total alkalinity, compared with the UNRM, or CNRM SNLs. However, CNRM does show an increase in solids ANC, which is most likely from destabilisation of aluminate in solution during CO_2 consumption of OH- and the subsequent precipitation of $Al(OH)_3$ (Equation 4); precipitated $Al(OH)_3$, then buffers pH at pH's <5.5, increasing solids ANC. Similarly, the Basecon™ and Hybrid materials also have increased ANC compared to both UNRM and CNRM.

the Cl concentration remains constant are made (Table 3) to account for the precipitation reactions, and alkalinity speciation changes occurring (Table 2). The pH and EC data for these standard solutions (Table 3) show clear relationships between the speciation of the cation and anion, and the pH and electrical conductivity of the solution.

Table 3. EC and pH results for the standardised analytical solutions.

Solution ID	Solution Strength	pH	E.C. mS/cm
NaOH	0.010 M	11.980	2.360
Na$_2$CO$_3$	0.005 M	10.800	0.960
NaHCO$_3$	0.010 M	8.740	0.900
NaCl	0.010 M	5.820	1.170
CaCl$_2$	0.005 M	5.640	18.100
MgCl$_2$	0.005 M	5.450	87.200

Data in Table 2 indicates that NaOH and Na_2CO_3 alkalinities dominate the UNRM, with a high EC, however CNRM halves the EC and changes alkalinity speciation. Table 3 data suggests that the EC change observed is consistent with a change from NaOH to $NaHCO_3$; changes between CO_3^{2-} and HCO_3^- speciation provide a negligible change in EC (Table 3). That is, a change in the anionic speciation from hydroxides to either carbonates or bicarbonates will reduce the sample E.C. by approximately 60 %, Similarly, where Basecon™ has been used the EC changes from NaOH dominated alkalinity, to a NaCl dominated residual systems is also consistent (Table 2 & 3). That is a change in anionic speciation from hydroxides to chlorides will result in a 50 % reduction in sample E.C., whereas a change from carbonates or bicarbonates to chloride systems will increase sample E.C. by

Table 2. Total and speciated alkalinity, pH and E.C. results for the neutralised and raw liquors and solids.

Parameter	Units	UNRM SNL	UNRM Solid	CNRM SNL	CNRM Solid	Basecon™ SNL	Basecon™ Solid	Hybrid SNL	Hybrid Solid
pH	units	13.14	10.91	8.66	8.38	7.55	8.27	7.55	8.26
		0.05	0.06	0.02	0.03	0.40	0.20	0.39	0.02
EC	ms/cm	116.10	7.40	59.60	1.50	52.90	8.20	76.20	48.20
		2.42	0.04	0.32	0.04	5.30	0.09	6.16	0.15
Tot Alk	g/L CaCO$_3$	38.30	-	36.70	-	0.15	-	0.30	-
		0.47	-	1.16	-	0.03	-	0.06	-
ANC (pH 4.5)	mole/kg	-	1.72	-	2.50	-	3.52	-	3.68
		-	0.02	-	0.10	-	0.20	-	0.14
OH	mg/L CaCO$_3$	3794.00	-	0.10	-	0	-	0	-
		436.00	-	0	-	0	-	0	-
CO$_3$	mg/L CaCO$_3$	16239.00	-	2858.00	-	1.37	-	2.87	-
		485.00	-	61.70	-	1.05	-	2.80	-
HCO$_3$	mg/L CaCO$_3$	6.40	-	38914.00	-	181.10	-	364.70	-
		0.90	-	1379.00	-	32.60	-	1.04	-

In all results Tables upper values for a parameter is the mean of three replicates, whereas the lower value is the standard deviation.

These data suggest that the addition of the Ca and Mg results in a precipitation of the alkalinity to increase solids ANC, whereas the addition of the CO_2 does not precipitate alkalinity. Furthermore, the speciation data (Table 2) indicate that the alkalinity in the CNRM changes from hydroxide dominated to bi-carbonate dominated, compared to near complete removal for Basecon™ and Hybrid.

To assist in the interpretation of the EC, pH and alkalinity results, a series of standard strength solutions where the Na concentration remains constant, and then another set where

approximately 22 %. Although, for the hybrid system, there is a slight increase in the EC over the Basecon™, suggesting higher residual concentrations of Ca and/or Mg in solution than for the Basecon™ system. These changes may reflect a change from complex-mineral precipitation in the direct Basecon™-system to simple-mineral precipitation in the hybrid-system, and solubility differences (Equations 1, 2, 4 & 5).

The results presented in Table 2 demonstrate a change in SNL, changes pH directly related to the change in speciation of the neutralised SNL, and the addition of CO_2 only changes speciation as predicted by alkalinity changes [40]. Consequently, the data collected in this study disagrees sharply with data of Jones *et al.* [36], where they see a substantial change in alkalinity concentrations. However, because this work used the same methodology as Jones *et al.*, the differences seen must show a discrepancy in the reporting of data. If the post-neutralisation data of Jones *et al.* [36] are considered there appears to be a 5 times difference between their data and data collected here, and suggests that the initial dilution of the samples to allow CO_2 bleeding into the suspension to occur, have not been worked back into the results, which then affects some interpretations made. Clearly, data here (Table 2 & 3) suggests that little or no Dawsonite precipitation occurs in solution, from CO_2 addition by gas diffusion process. However, it may be that the addition of CO_2 in liquid form (as indicated by Cooling *et al.* [ref] as the most efficient means) may well allow the development of suitable geochemical gradients to allow Dawsonite formation to occur and allow a substantial reduction in soluble alkalinity.

3.3 Solids Analysis

EDAX SPOT analysis (Table 4) suggests that there are distinct groupings similar to the groupings delineated by the alkalinity results. The data suggest that UNRM and CNRM form one group while the Basecon™ and Hybrid samples form a second. This separation is primarily due to the higher Ca, Mg and Cl concentrations of the Basecon™ and Hybrid because of the addition of Ca and Mg-chloride salts during Basecon™ neutralisation, that are precipitated to the solids. Basecon™ and Hybrid materials have increased Ca and Mg, which is from the precipitation of minerals (Equations 1, 2, 4 & 5) for Basecon, than the more simple minerals (Equation 5) for CNRM. Contrary to the increased Ca and Mg, there is a drop in Na, and Fe concentrations, from a dilution effect predicted by Equations 1, 2 & 5. However, with only 15 spot analyses, the standard point counting statistics indicates that at least 200 data points are required for statistical robustness [39], therefore the EDAX data can only be indicative.

Table 4. Summary of the EDAX mineralogy results.

Parameter	Units	UNRM Solid	CNRM Solid	Basecon™ Solid	Hybrid Solid
EDAX Al	%	13.99	14.73	17.26	16.32
		6.09	3.95	9.97	6.09
EDAX Ca	%	1.93	1.94	5.54	3.14
		3.13	0.88	11.51	8.98
EDAX Cl	%	0.54	0.26	3.60	4.30
		0.20	0.21	2.00	2.41
EDAX Fe	%	41.53	38.11	24.54	31.60
		17.38	18.26	14.78	18.92
EDAX Mg	%	0.03	0.05	2.66	1.68
		0.13	0.07	1.70	0.91
EDAX Na	%	4.68	4.00	2.27	2.26
		2.00	2.58	1.91	1.72
EDAX S	%	0.66	0.60	0.61	0.51
		0.30	0.40	0.35	0.32
EDAX Si	%	5.64	7.34	7.32	7.36
		2.93	5.03	4.24	5.32
EDAX Ti	%	2.87	3.28	2.84	2.74
		1.63	1.54	1.54	1.63

3.4 Metal and Phosphate Loading Capacity

Data from the metal and phosphate loading tests (Table 5) do not show the distinct sample grouping shown by the alkalinity data (Table 2). The metal data indicate that metals are more strongly removed to the UNMR, because of an apparent greater pH rise. Although all metals are removed to similar extents to all materials except Mn and Ni, which are removed at a higher proportion than for CNRM, Bauxsol™, or the hybrid material. These observations would tend to suggest that the pKa of hydration in the formation of species that are removable from solution occur [41]. Furthermore, the metals data (Table 5) suggests that the solids have not reached a complete saturation of available removal sites, because there is near complete removal of all metals.

Because there is an underlying core mineralogy to all the treatments, it is likely that much of the metal binding is related to this underlying mineralogy, and the differences in the minerals present after neutralisation are responsible for some of the metal binding differences observed. For example, even raw bauxite is a strong metal binding system, to utilise the fine hematite and gibbsite adsorptions [42]. However, the removal of Al from per-aluminous hematite during alkaline-digestion seems to increase the metal binding [41-43]. Some metal removal mechanisms will change because of the changes in the solution chemistry and the species changes in the neutralisation (Table 3). Hence because, UNRM will be most affected by hydroxide (Table 3) it is likely that metal removal will be dominated by precipitation of amphoteric hydroxide precipitation, whereas CNRM being bi-carbonate dominated is more likely to precipitate metals as carbonates. These trends do appear in the data (Table 5) where hydroxide dominated metals (e.g. Al, Fe, Mn & Ni) are more readily removed by UNRM, but for CNRM, stronger carbonate bound metals (e.g. Cu & Zn) are more readily bound.

Table 5. Summary of the Metal and Phosphate Loading Capacity test results.

Parameter	Units	Synthetic AMD	UNRM	CNRM	Basecon™	Hybrid
pH	units	2.360	7.310	6.890	6.870	6.670
		0.010	0.010	0.040	0.006	0.020
Al	mg/L	350.000	0.10	0.147	0.197	0.250
		30.000	0	0.006	0.057	0.044
As	mg/L	9.330	0.180	<0.100	0.700	<0.100
		0.056	0.010	0	0.010	0
Cd	mg/L	20.670	0.100	0.630	0.470	2.630
		2.310	0.010	0.110	0.030	0.150
Cu	mg/L	102.000	0.220	0.210	0.100	0.110
		9.500	0.030	0.051	0.006	0.010
Fe	mg/L	397.000	0.120	0.150	1.360	<0.100
		25.200	0.010	0.050	1.860	0
Mn	mg/L	112.000	13.000	59.000	39.000	58.000
		8.500	2.650	4.000	1.000	2.000
Ni	mg/L	99.700	5.900	36.300	19.000	26.700
		7.500	1.060	5.510	1.000	1.150
Zn	mg/L	101.000	0.690	<0.100	<0.1.000	0.940
		5.000	0.140	0	0	0.630
P	mg/L	28.000	21.300	23.700	0.460	0.450
		0	1.160	0.580	0.006	0.050

Clark [41] and subsequent work [e.g. 4 13-15, 31, 34, & 43], have shown that the binding of metals to Bauxsol™ solids over very large pH ranges is a function of large variety of charged minerals surfaces that show differential charge (i.e. charge sign and density changes with pH). McConchie *et al.* [4], note that there are some 30 mineral species within Bauxsol™, more than

in UNRM. It is highly likely that the increased range of mineral species in Bauxsol™ provides an enhancement of this binding. Similarly, the precipitation of carbonates in the Hybrid material will also increase mineral diversity and improve metal removals. Furthermore, Clark *et al.* [43], using Mössbauer analysis determined that the mean grain size of the hematite crystallites in red muds was 122Å, which provides very high surface charge to mass rations and make them ideal for metal binding. However, the authors [43] go on to note that, binding is not by adsorption alone and that crystal growth, new mineral precipitation and, intra-crystalline diffusion provide the majority of metal binding, and that adsorptive charge attraction provide the mechanism to attract dissolved metals to these reactive mineral surfaces.

The data collected here seem to indicate that UNRM and CNRM, are precipitating metal species as simple amphoteric hydroxides and carbonates from the soluble alkalinity, but that the Basecon™ and the Hybrid material have a much more complex metal removal process because of the alkalinity precipitations that occur prior to metal loading. It is highly likely that more complex metal removal will reflect in a resistance to liberate metals from the solids, using a test like TCLP.

The phosphate results (Table 5) do show a clear distinction between the UNRM and CNRM from Basecon™ and Hybrid materials. For P removal the Basecon™ and Hybrid samples greatly outperform the UNRM and CNRM samples with greater than 98% P removed from solution; cwf 20-25%. The neutralisation of the soluble alkalinity for both Basecon™ and Hybrid materials requires the addition of Ca and Mg in a treatment solution, and the data suggests that the high Ca and Mg loadings of these two materials give the corresponding increase in P binding. Higher P loadings data are recorded when UNRM is neutralised using gypsum (Alkaloam™) than for UNRM [4, 13-15, 31, 34. 43]. Hence, a major mechanism for P removal to the solids would appear to be the precipitation of poorly soluble Ca- and Mg-phosphates, and such phosphates, although of low water solubility, remain plant available. [4, 13-15, 31, 34. 43].

The TCLP release of metals from loaded solids indicates that there is a distinction between the UNRM and CRNM, and the Basecon™ and Hybrid neutralised materials (Table 6). Furthermore, there seems to be some distinction between the Hybrid and the Basecon™ materials, and the UNRM and CNRM materials as well. The metals that denote the distinction between the UNRM and CNRM, and the Basecon™ and Hybrid neutralised materials are Zn, Ni, Mn, Fe, and Cu. The further distinction between the Hybrid and the Basecon™ material appears for the metals Al, Cd, Cu and Fe, whereas the distinction between the UNRM, and CNRM appears in As, Ni, & Fe release (Table 6).

Zn for UNRM and CNRM is leached at concentrations of about 8mg/L, but for Basecon™ and Hybrid materials, the leaching is reduced to about 4mg/L. Similarly, Ni reduces from about 4mg/L to 2mg/L, Mn falls from about 10mg/L to 7mg/L, whereas Fe falls from > 8mg/L to < 4mg/L, and Cu falls from about 5.5mg/L < 3.5mg/L. The Basecon™ material leaches only about half the Al, Fe and Cd of the Hybrid material, whereas Cu leaching in the hybrid material is about half of the Basecon™ material. For the UNRM As leaching is about more than three times that for CNRM, whereas Fe, and Ni leaching is more than twice that of the CNRM. It is likely that these leaching behaviours (Table 6) are a result of the way that alkalinity converts and removes from the system, and how complex the mineral precipitates are from the alkalinity conversions. In addition, these mineral precipitates will also influence the final pH of the solution from which metal removal occurs (Table 5).

Table 6. Summary of the Metal Loading Capacity TCLP test results.

Parameter	Units	UNRM	CNRM	Basecon	Hybrid
Al	mg/L	790.00	793.00	380.00	763.00
		140.00	42.00	87.00	112.00
As	mg/L	0.54	0.15	0.09	0.14
		0.15	0.05	0.05	0.02
Cd	mg/L	3.07	2.90	0.97	2.20
		0.38	0.26	0.15	0.26
Cu	mg/L	6.40	5.40	3.50	1.87
		0.78	0.40	0.61	0.06
Fe	mg/L	18.00	8.40	1.97	3.43
		3.61	0.70	0.95	0.78
Mn	mg/L	10.97	9.50	7.23	7.30
		0.90	0.78	0.57	0.87
Ni	mg/L	4.13	2.47	1.70	1.43
		0.57	0.21	0.26	0.06
Zn	mg/L	8.67	8.37	4.93	3.60
		0.61	0.74	0.81	0.00

For any industry the definition of sustainability must be the elimination of waste materials, simply because if there are no wastes, the only outputs from the industry must be products. The alumina industry produces large volumes of intractable waste each year, and reuse of these wastes reduces liability, costs, and environmental footprint. The three neutralisations investigated provide some impact into the equation of sustainability, but not all are as successful as some. UNRM must be stored as a scheduled waste because of the Basel convention, prohibits transport across state boarders [11].

Although carbonation of UNRM converts alkalinity and reduces pH (CNRM), most of the alkalinity remains highly soluble and in the surface waters in sodium forms (Table 2). UNRM will draw CO_2 from the atmosphere naturally, but this may take several hundreds of years to fully accomplish. In addition, few jurisdictions allow the discharge of surface waters with alkalinities >200mg/L [45], hence waters need to evaporate within ponds, which means that UNRM and CNRM, will retain high sodium contents, making them unsuitable for environmental use [45]. It is also unlikely that CNRM would allow a reclassification of UNRM to product status, especially under current European legislation.

The conversion of UNRM to Bauxsol™ using Basecon™ is considered a manufacturing step because the ratios of Ca and Mg to change mineral precipitations and tailor composition. Similarly, the Hybrid material, because it uses the Basecon™ precipitations [31], should classify it as a product rather than a "Green Waste" or "Recycled Material". More importantly for Basecon™ and Hybrid materials, is that alkalinity in the water precipitates (Table 2) such that the issuing of discharge permits for pond waters are more likely [45], and that sodicity of the solids is reduced as waters remove soluble sodium. Consequently, Basecon™ and Hybrid material are more acceptable for application in environmental remediation than CNRM or UNRM.

Even if CNRM could gain ready acceptance by regulators for environmental remediation work, there are several applications where it has a substantially reduced effectiveness. These applications are where retention of phosphorous is desired. Table 4 shows that removal rates of P to CNRM compared to Basecon™ and Hybrid material is substantially reduced, hence to control the same quantity of phosphorous, nearly 4 time the dose rate is required. Such applications for P removal are in sewage treatments, some soil remediation and in the control of farm effluents and fertiliser applications. In addition, where metal binding is required CNRM does not perform as well as

Basecon™ or Hybrid materials, especially for Zn, Cd, Fe and Cu. Cd, which is a known toxic contaminant, can be present in many fertilisers especially those derived from guano deposits, and a weak retention of Cd is detrimental to this sort of application. Hence, of the materials investigated here the Basecon and Hybrid material provide the best means of reuse in environmental applications.

Of the Basecon™ and Hybrid materials, both perform remarkably similar except for the TCLP leaches. The Hybrid material does not retain Cd nor Al as well as the Basecon™ material under the pH 2.88 TCLP leach. However, calculating from the alkalinity speciation data Table 2 indicates that 39 mmoles of CO_2/kg of red mud are required to convert the alkalinity from Hydroxide-carbonate dominated to bi-carbonate dominated systems (Equations 4 & 5). This is equivalent to 17.3 kg of CO_2/Ton of red mud or to about 1.2 MTon of CO_2/year across the industry, given current production values. In addition, experimental setups indicate that at 200 mL/min for 25 minutes of CO_2 bleeding into 300g of red mud that 32.7 g/kg, or kg of CO_2/Ton of red mud is consumed, suggesting that a diffusive bleed of CO_2 into red mud is only about 50% efficient. Unfortunately, the CO_2 conversion requirements obtained here are not easily compared to those of Cooling *et al.* [35], because their data is in kg/kL, no slurry density data are presented, nor is any alkalinity data presented, and the lowest pH that their data is pH 8 (pH of ≈7.5). Despite the lack of suitable Cooling *et al.* [35] data, a Bauxsol™ slurry at 60% solids gives a bulk density of about 1.4 (Clark unpublished data), which provides a CO_2 consumption of 24.2 kg/kL, which is comparable to those of Cooling *et al.* [35]. Given that the Hybrid material displays similar geochemical behaviour to the Basecon™, there is the added benefit of permanent sequestration of about 17.3 kg CO_2/Ton red mud (24 kg/kL) to the solids.

4. Conclusions

Red mud is the largest volume industrial waste in the world, with most going to large impoundments, presenting major difficulties for remediation or re-use due to its high pH, alkalinity, sodium content and sheer volume. The difficulties in commercialising technologies and subsequent applications on the reuse of red mud meet regulatory resistance. Although some applications have managed a measure of commercial success, none have yet reached a scale suitable to substantially impact the annual global output, let *al.*one the stockpiles of past years. However, conversion of material from toxic, caustic scheduled waste, to more benign forms for the safer storage of material must be considered a step in the right direction.

Investigations here show that the neutralisation techniques form two distinct geochemical groups: UNRM and CNRM, and the Basecon™ and Hybrid material. The UNRM and the CNRM have similar total alkalinities and phosphate loading capacities (<25 % removal). However, the alkaline species remain almost entirely soluble and convert from the hydroxide-carbonate dominated UNRM to bicarbonate-carbonate dominated for CNRM; pH falls from 13.2 to 7.5 for CNRM. The Basecon™ and Hybrid materials have similar total and speciated alkalinities (≈ 0.25g/L as equivalent $CaCO_3$) in the residual liquors. Solution pH and E.C. are similar to the CNRM material, whereas, although the phosphate loading capacities for Basecon™ and Hybrid materials are similar to each other (>98 % removal), they are substantially greater than those for either the UNMR or CNRM are (≈25%).

This study demonstrates the potential to combine several of the existing red mud treatment technologies into a single sequential process that consumes CO_2 by the conversion of soluble hydroxides to soluble carbonates and the subsequent precipitation of insoluble carbonates and bicarbonates. The Hybrid solid has a near-neutral pH (8-8.5) and is suitable for environmental remediation. Hybrid SNL residual liquor disposal or re-use options are enhanced by the precipitation of the alkalinity and the reduction in pH from >13 to <8.5. Hybrid material at this stage of our investigations appears to provide some environmental advantage to Basecon™ because of an additional ≈17 g/kg CO_2 consumption during the alkalinity transformation.

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