

Alkalinity conversion of bauxite refinery residues by neutralization

M. Johnston*, M.W. Clark, P. McMahon, N. Ward

Environmental Science and Management, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia

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ABSTRACT

Red mud remains the largest environmental issue for the alumina industry due to its high pH (>13), fine-grained nature (>90% is <10 μm), elevated sodium concentration (>50 g/kg), and soluble alkalinity (≈30 g/kg as equivalent CaCO₃), which reduce the transport and reuse options of red mud. The neutralization of red mud provides potential reuse options because neutralization lowers pH, increases grain-size (e.g., coagulation), and precipitates or converts alkalinity. This paper investigates the geochemistry of 3 treatments of a red mud to affect neutralization and potentially convert materials from a waste material to a resource. This study investigates two commonly used neutralization techniques, a CO₂-neutralized red mud (CNRM), a Basecon™-neutralized red mud (Basecon™), and a more novel approach of a CO₂-neutralization followed by a Basecon™-neutralization (Hybrid) to understand the effects that these treatments have on neutralization process. Data indicate that the neutralization techniques form two distinct geochemical groups when discriminated on total alkalinity alone, that is treatments with, and treatments without alkalinity precipitation. However, each treatment has distinct alkalinity speciation (hydroxide-dominant or carbonate/bicarbonate dominant) and residual Ca, Mg and Al in the treatment solution. Similarly, solids produced differ in their reaction pH and ANC, and contrary pH and ANC, a contrary to other studies, Dawsonite was not seen to precipitate during any neutralization. However, despite this approximately 17 g/kg CO₂ was sequestered during CNRM and hybrid neutralizations and all treatments increased either the transport or reuse options of red mud in some way.

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1. Introduction

The Bayer alumina extraction process takes bauxite, typically containing gibbsite (Al(OH)₃·3H₂O), diaspore (β-AlOOH), boehmite (γ-AlOOH), and hematite (Fe₂O₃), that is digested in a caustic liquor (pH > 13) of Na and Ca-hydroxides. This digestion, used since 1890, produces two output streams, liquor pregnant with alumina that is for alumina precipitation, and a solid residue (red mud) for disposal. This waste residue is initially slurry, with a moisture content ranging from 50–70%, containing residual caustic liquor that is often re-cycled through the plant after filtration [1–3].

Annually some 70 million tonnes of red mud is produced globally [4,5] at a rate of about 1.1–6.2 tons produced per tonne of alumina. Red mud presents a major ecological and economic problem worldwide due to because it contains a high sodicity (>50 g/kg), high pH (>13), alkalinity (>20,000 mg/L as equivalent CaCO₃), and a wide range of potentially mobile trace-metals [3,4,6–10]. Consequently 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 of red mud continues to go to

surface impoundments for long-term storage. The adverse chemistry outline means that red mud is listed as a contaminated waste under the Basel Convention [11,12], which limits transportation for storage, disposal, or treatment applications and reuse options [3,4,7–9,13–16].

Despite the adverse chemistry red mud has a high acid neutralization capacity (ANC; up to 10 mol H⁺/kg, mainly via OH⁻ and CO₃²⁻), and contain fine-grained iron oxy-hydroxides which provide an ability to bind many cationic and anionic species. Hence red mud and some neutralized forms have been investigated and used to treat acid mine drainage (AMD), acidic sediments and soils, industrial effluents; and as a landfill covers, odour reducers, catalysts, road base, fertilizer filler, permeable reactive barriers, clay capping, ceramics, geo-polymers, construction materials and synthetic soils [9,14,15,17–26].

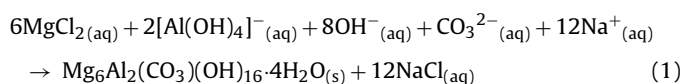
Many of the uses for red mud are capable of reducing the volume of waste mud and producing useable products, however, the use of red mud is restricted by the Basel convention, and to remove these restrictions some form of neutralization is required, primarily to reduce the pH to <10.5 where pH 7–9 is the desired end-point. Currently there are three main neutralization methods that have the greatest potential to provide environmentally sustainable outcomes including, seawater neutralization, Basecon™ neutralization and CO₂ gas re-circulation. Each method produces a

* Corresponding author. Tel.: +61 2 6620 3487; fax: +61 2 6626 9499.
E-mail address: max.johnston@scu.edu.au (M. Johnston).

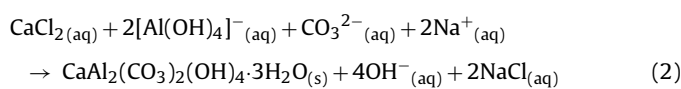
final product with improved storage, transport and reuse options over raw red mud [14,27–29] by the lowering of pH.

Seawater neutralization of red mud is used by some coastal refineries (e.g. Queensland Alumina; QAL Ltd.), involves the addition of excess seawater (up to 20 times the volume of mud) to precipitate the soluble hydroxides and carbonates as insoluble hydroxides ($\text{Mg}_3(\text{OH})_6$), carbonates (CaCO_3 and MgCO_3) and hydroxy-carbonates ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$, $\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4\cdot 3\text{H}_2\text{O}$); residual seawater is then discharged back into the ocean after use [29,30]. Seawater neutralization lowers liquor pH and alkalinity, allowing discharge, and the residual mud can be stored more safely or reused in a wider range of applications. Red mud neutralized via the Basecon™ procedure [31] is Bauxsol™, and because Basecon™ neutralization is regarded as a manufacturing process, Bauxsol™ is classified as an environmentally non-hazardous product in several countries [32,33]. The Basecon™ procedure is similar to a seawater neutralization, but uses artificial Ca and Mg-rich brines >20 times the concentration of seawater to improve efficiency and to allow variation of the Ca:Mg ratios to favour particular mineral precipitates [4,13,14,15,31,34]. The key chemistry of both Basecon™ and seawater neutralization are the precipitation of hydrotalcite and para-aluminohydrocalcite (Eqs. (1) and (2)), although other reactions are also possible (Eqs. (3) and (4)).

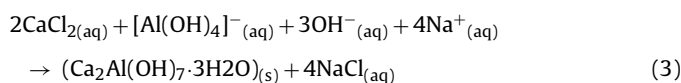
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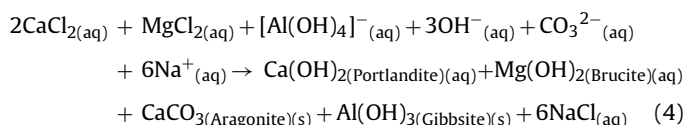
Para-aluminohydrocalcite



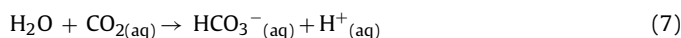
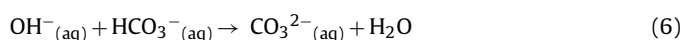
Hydrocalumite



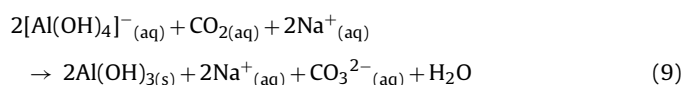
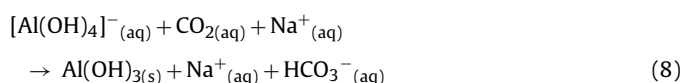
Gibbsite, Aragonite, Portlandite, and Brucite



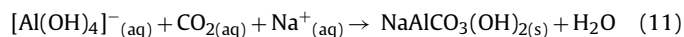
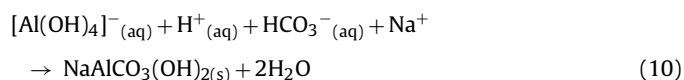
A CO_2 neutralization utilises the reaction of CO_2 with hydroxide to form bicarbonate and the reversibility of key alkalinity reactions between hydroxide, carbonate and bicarbonate (Eqs. (5)–(7)). The hydroxide (OH^-) component of the red mud may then be converted to carbonate and bicarbonate, thereby lowering liquor pH to <8.5. The innovative nature of this neutralization is the stable-mineral sequestration of CO_2 to reduce atmospheric and industrial carbon dioxide emissions, that may provide additional benefits such as trapping metal and metalloid contaminants.



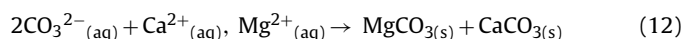
The red mud liquors produced by neutralization are not simple hydroxide solutions, as much of the hydroxide is involved in the solubilisation of residual aluminium as aluminate ($[\text{Al}(\text{OH})_4]^-$). The consumption of free hydroxide from the aluminate anion will also cause precipitation of alumina ($\text{Al}(\text{OH})_3$) by:



Consequently, soluble carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions should be the dominant products of the CO_2 neutralization process, without substantially adding to or reducing total alkalinity of the mud [35]. However, previous work on CO_2 neutralization suggests that the precipitation of Dawsonite occurs [15,27,36] by either of the following generalised equations:



The simple chemistry of Eqs. (8) and (9) would suggest that the CO_2 neutralization [35] mostly affects alkalinity speciation rather than alkalinity solubility; hence there is further potential to combine CO_2 neutralizations with a Basecon™ neutralization [35] to then precipitate residual alkalinity. The resulting chemistry is unlikely provide the complex mineral precipitation of a direct Basecon™ neutralization, but rather a much simpler chemistry (Eq. (12)).



Although a composite neutralization has been made previously [35], only a cursory investigation of the chemistry of the products was made. However, since each neutralization technique outlined has potentially profound effects on the chemistry of the residual solids and liquor, these neutralization techniques should be investigated further. Consequently, this paper investigates and compares alkalinity conversion of a bauxite refinery residue neutralized by these 3 different methods. The paper documents the changes in alkalinity between un-neutralized (UNRM), a Basecon™-neutralized (Basecon™), a CO_2 -neutralized red mud (CNRM), and CO_2 -Basecon™-neutralized red mud (Hybrid) liquor, and how these changes reflect mineral precipitation and mechanisms of neutralization.

2. Methods

The raw red mud sample used throughout the experimental process originated from an Australian plant, and was supplied from the last washer underflow. The mud was thoroughly homogenised and a sub-sample was oven dried at 65 °C for 1 week to provide the initial moisture content. The untreated red mud and all neutralizations used an initial solid: water ratio of 1:5 (300 g equivalent dry material: 1500 mL de-ionized water) 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. [37]. A slight modification to Jones et al. [37] made here is a CO_2 diffusion for 25 min rather than 20 min, which was found to substantially reduce pH reversion. Table 1 summarises the actual steps used as apart of each neutralization technique; three separate replicates of each neutralization were made as independent samples to produced statistically valid data.

The treatment supernatant liquor (SNL) was decanted for alkalinity, pH, EC, and dissolved metals analysis. Residual solids were dried and crushed in the same manner as the red mud sample for ANC, pH and EC analysis.

Liquor from a 1:5 solid:reagent-water extraction (tumbled at 15 rpm for 1 h then centrifuged at 3000 rpm for 10 min) is analysed for pH with probes calibrated to a slope of >98% and an asymmetry of <0.1 using pH 4, 7 and 10 buffer solutions, and electro-conductivity (EC) with probes calibrated to $K=1.00$

Table 1
Neutralization procedure used for the four samples tested.

Parameter	UNRM	CNRM	Basecon™	Hybrid
Initial solid mass (g)	300	300	300	300
Initial DI water addition (mL)	1500	1500	1500	1500
Initial mix time (min)	30	30	30	30
CO ₂ gas flowrate (mL/min)	na	200	na	200
CO ₂ diffusion time (min)	na	25	na	25
CaCl ₂ ·2H ₂ O salt (g)	na	na	21.74	21.74
MgCl ₂ ·6H ₂ O salt (g)	na	na	132.42	132.42
Final mix time (min)	30	30	30	30
Settlement	Overnight	Overnight	Overnight	Overnight
SNL filtration	0.45 μm paper	0.45 μm paper	0.45 μm paper	0.45 μm paper

Table 2
Total and speciated alkalinity, pH, EC and dissolved metals data for the neutralized and raw liquors.

Parameter	Units	UNRM		CNRM		Basecon™		Hybrid	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
pH	Units	13.14	0.05	8.66	0.02	7.55	0.40	7.55	0.39
EC	mS/cm	116.1	2.42	59.6	0.32	52.9	5.30	76.2	6.16
Total Alkalinity	g/L CaCO ₃	38.3	0.47	36.7	1.16	0.15	0.03	0.30	0.06
OH	mg/L OH ⁻	3794	436	0.1	0.0	<0.1	0.0	<0.1	0.0
CO ₃	mg/L CO ₃ ²⁻	16239	485	2858	61.7	1.37	1.05	2.87	2.80
HCO ₃	mg/L HCO ₃ ⁻	6.40	0.90	38914	1379	181.1	32.6	365.7	1.04
Al	mg/L	534	2.71	1.59	0.33	0.05	0.04	0.07	0.05
Ca	mg/L	1.0	0.23	0.1	0.007	356	14.2	466	18.4
Mg	mg/L	<0.1	<0.1	<0.1	0	5219	34.4	6482	56.1
Na	mg/L	7447	18.1	7536	62.3	7694	78.9	7373	94.2

(±0.05) in a 2.76 mS/cm solution. A 30 mL sub-sample of unfiltered SNL for raw or the neutralization liquors were titrated against 0.1 N HCl, recording incremental volume and pH. Acid concentration, pH, EC, temperature and titration data (millilitres titrant added and pH) entered into USGS Web-based Alkalinity Calculator (<http://or.water.usgs.gov/alk/>) where total, and speciated alkalinity is calculated using the fixed-end-point (to pH 4.5) method for reporting; samples are filtered at pH 7.5 to remove the Al-precipitates that form. The acid neutralizing capacity (ANC) of residual solids is determined by titration of a 1:10 solid: water suspension with 0.1 M HCl to pH 4.5.

Treatment SNL's are analysed for dissolved metals (Al, Ca, Mg and Na) by taking a 10 mL aliquot and passing through a 0.45 μm cellulose-acetate filter prior to acidification to pH 1, using concentrated nitric acid. Prepared SNL fractions are analysed by ICP-MS at a registered, nationally accredited laboratory independent of the researchers, 2 sample blanks, 2 spiked samples and 1 artificial standard were included as external QA/QC checks, in addition to the internal QA/QC check samples of the analysis laboratory.

The geochemical data produced is analysed statistically using SPSS 14 (for PC) to validate the normality of the data and determine sample groupings where present. Non-parametric tests were chosen because of the non-normal distribution of data and $n = < 30$. The Kruskal–Wallace t -test (2-tailed) is used to determine if the rank totals for all parameters are different for all experimental groups, and can only determine the overall differences (if any) between populations (sample types). The Mann–Whitney U -test (1-tailed) is used to determine the difference (if any) between pairs of samples for each parameter (equivalent to a parametric t -test) across all parameters (liquor and solid).

3. Results and discussion

Table 2 summarises the pH, EC, total and speciated alkalinity, and dissolved metals data for all sample SNL's. The data shows distinct changes in the pH and EC between the UNRM SNL and the three neutralized SNL's. The application of any neutralization tech-

nique to UNRM resulted in a substantial decrease in the pH (13.1 to <8.7) and EC (116 to <76 mS/cm). However, such changes in the total alkalinity of the SNL are not observed for all the neutralization techniques. For example there is no substantial change in the total alkalinity from the UNRM (38.3 g/L CaCO₃) by the CNRM neutralization (36.7 g/L CaCO₃). However, the Basecon™ (0.15 g/L CaCO₃) and Hybrid (0.3 g/L CaCO₃) neutralization methods show a substantial reduction in SNL total alkalinity compared to UNRM and CNRM, demonstrating the precipitation of alkaline minerals from solution.

Investigation of the alkaline speciation reveals a substantial change between the UNRM and the neutralized samples. Hydroxide is virtually eliminated from the UNRM (3794 mg/L) to <0.1 mg/L for all treatments (Eq. (5)) and carbonate is reduced by >80% from 16,239 mg/L (UNRM) to 2858 mg/L by CNRM, and by >99% to <3 mg/L for both Basecon™ and Hybrid. The bicarbonate fraction is perhaps the most indicative of the mineral changes occurring during neutralization, with CO₂ neutralization converting both the hydroxide and carbonate fractions of the UNRM to soluble bicarbonate (Eq. (5)). Hence the high CNRM bicarbonate concentration (38,914 mg/L), whereas the Basecon™ and Hybrid convert and precipitate the alkaline species (Eqs. (1)–(4) and (12)), consequently the soluble bicarbonate concentration is low (<370 mg/L). Comparing the Basecon™ to the Hybrid shows the Basecon™ (181 mg/L bicarbonate alkalinity) is around half the bicarbonate alkalinity concentration of the Hybrid (366 mg/L), suggesting a more complete precipitation of alkalinity, most likely as complex aluminocarbonate minerals (Eqs. (1)–(4), (8) and (9)), rather than the simpler carbonate and aluminohydroxide minerals (Eqs. (8) and (9), (12)).

Dissolved metal data (Table 2) indicates that a small concentration of Ca is present in the UNRM, most likely from the lime regeneration of hydroxide used by many refineries, but this is mostly removed during carbonation and alkalinity conversion in CNRM. However in the Basecon™ and Hybrid liquors substantial Ca and Mg remain from the treatment brine used for alkalinity precipitation (Table 2). The Hybrid has a residual Ca and Mg concentration about 30% greater than Basecon™, suggesting that the simplified precipitation products of the CO₂ neutralization (Eq. (12)) are more

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

Solution ID	Solution strength	pH	EC (mS/cm)
NaOH	0.01 M	11.98	2.36
Na ₂ CO ₃	0.005 M	10.80	0.96
NaHCO ₃	0.01 M	8.74	0.90
NaCl	0.01 M	5.82	1.17
CaCl ₂	0.005 M	5.64	18.1
MgCl ₂	0.005 M	5.45	87.2

soluble than the direct, and more complex mineral precipitates (Eqs. (1)–(3)) of Basecon™.

Soluble Al drops by >99.5% from UNRM to CNRM, but is further reduced from the addition of Mg and Ca in Hybrid liquor (Table 2). This suggests the increased divalency provided by the addition of Ca and Mg improves Al(OH)₃ removal most likely by flocculation, or by co-precipitation with the carbonates (Eq. (12)). However, the Basecon™ treatment has the lowest Al concentration, which is about half of the hybrid solution, and only about 2% of the CNRM liquor (Table 2). These differences suggest that the 1-step mechanism for Al and alkalinity removal (Eqs. (1)–(3)) are much more efficient and produce minerals with much lower solubility products than the 2-step removal of Al and alkalinity (Eqs. (8), (9) and (12)). Moreover, the reductions in soluble Al during CO₂ additions is not paralleled by any significant reductions in soluble Na, suggesting that the precipitation of Dawsonite (Eqs. (10) and (11)) is not occurring, or it is very minor in comparison to Al(OH)₃ precipitation; all sodium data are all within ±5% error of each other any reductions are obscured by the intra-sample variability of the analyses. These data strongly suggest that no Dawsonite precipitation is occurring in either CRNM, or the Hybrid neutralizations, and indicate that critical thresholds in solution chemistry are not crossed when CO₂ is added, such that Eqs. (10) and (11) do not become dominant.

Statistical analyses using both the Kruskal–Wallace and Mann–Whitney tests determined that all sample types were overall statistically different ($p < 0.05$; i.e., there are four geochemically individual products with no statistical grouping between treatments across all parameters). However, a closer examination of just total alkalinity does indicate that there are 2 treatments groups, treatments that precipitate significant concentrations of alkalinity (Basecon™ and Hybrid), and treatments that are non-precipitative of alkalinity (UNRM and CNRM).

To assist EC, pH and alkalinity interpretation of the results in terms of dissolved and precipitated minerals, a series of standard strength solutions were made (Table 3). Solutions are chosen based on the most likely minerals to be found in, or added to, the original red mud. The variation in EC from anion changes when Na concentration remains constant are useful to compare UNRM and CNRM neutralizations, where only the anion is changed substantially and Na is the dominant cation. The variation in EC with cation changes when the Cl concentration remains constant are useful for interpreting Basecon™ and Hybrid data, where both Ca and Mg are added as chloride salts and the potential variation in precipitation rates of both cations are relevant to the interpretation of the mineral products; NaCl solution provides a link between cation and anion solutions. The pH and EC data for these standard solutions

(Table 3) show clear relationships between the speciation of the cation and anion, the pH, and electrical conductivity of the solution. Comparison of sample pH and EC values to those in Table 3 can indicate which chemical equations may be occurring, and hence which minerals may have precipitated or remain in solution.

These data indicate that changing the cation has the greatest impact on EC with Mg imparting about a 75 times increase from NaCl (1.17 mS/cm) to MgCl₂ (87.2 mS/cm), whereas Ca raises EC some 15 times from NaCl to CaCl₂ (18.1 mS/cm). Whereas, changing the anionic species from hydroxide to either a carbonate, or bicarbonate result in about a 60% drop in EC, similarly changing the anionic species from hydroxide to chloride reduces EC by about 50%. All chloride solutions were of similar pH (5.5–5.8) regardless of cation, but the hydroxide has the highest pH (12), with the carbonate (pH 10.8) and bicarbonate (pH 8.7); recorded pH's are close to expected equilibrium pH's of 10.2 for carbonate and 8.3 for bicarbonate.

Comparison of sample EC data (Table 2) with data in Table 3 suggests that NaOH and NaCO₃ alkalinites dominate the UNRM, with a high EC, however the CNRM halves the EC and changes alkalinity speciation (Table 2). This suggests that the EC change observed is consistent with a change from NaOH to NaHCO₃⁻, however changes between CO₃²⁻ and HCO₃⁻ speciation provide a negligible change in EC (Tables 2 and 3). When a Basecon™ neutralization is used the liquor changes from a NaOH dominated system to a NaCl dominated system where a change in anionic speciation from hydroxides to chlorides resulted in the expected 50% reduction in sample EC (Tables 2 and 3). For the Hybrid system, there is an increase in the EC over the Basecon™, suggesting higher residual concentrations of Ca and/or Mg in solution (Table 3) than for the Basecon™. The changes in EC through an increase in residual Ca and Mg, may well reflect the change between the complex-mineral precipitation products of Basecon™ and the simpler and/or amorphous-mineral precipitation products in the Hybrid conversion (Eqs. (1), (2), (4) and (5)).

The pH results presented in Table 3 demonstrate a change in liquor pH directly related to the change in anion speciation of the neutralized SNL from hydroxides to bicarbonates, as demonstrated by data in Table 2. The addition of CO₂ only changes alkalinity speciation, and not alkalinity solubility, from Na-hydroxide (pH 13.1) to a Na-bicarbonate/Na-carbonate (pH 8.7) as suggested by the alkalinity changes alone [39]; CO₂ neutralizations where pH stabilised at 10.6 after a 20 min diffusion time will result in a Na-carbonate dominated system.

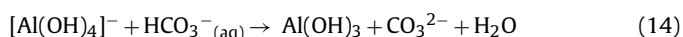
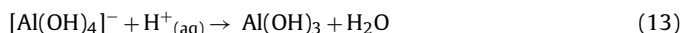
However, despite no substantial change in liquor alkalinity, CNRM does show an increase in solids ANC (Table 4), which is most likely from destabilisation of aluminate in solution during CO₂ consumption of OH⁻ and the subsequent precipitation of Al(OH)₃ (Eq. (8)); precipitated Al(OH)₃, dissolves then buffers pH at pHs < 5.5, increasing the apparent solids ANC, which is titrated with acid to pH 4.5. In addition, the fine-grained iron oxy-hydroxides are colloidal in nature, and reducing pH from 13 to 8, will change the surface charge on the surface from negative to positive (iso-electric point for hematite is 7–8.5 [38]), which allows the binding of some hydroxide to the mineral surfaces, thereby increasing solids ANC further. Similarly, the Basecon™ and Hybrid materials show an increase in ANC compared to both UNRM and CNRM. These data

Table 4
pH, EC and acid neutralizing capacity (ANC) results for the neutralized and raw solids.

Parameter	Units	UNRM		CNRM		Basecon™		Hybrid	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
pH	Units	10.91	0.06	8.38	0.03	8.27	0.20	8.26	0.02
EC	mS/cm	7.40	0.04	1.50	0.04	8.20	0.09	48.2	0.15
ANC (pH 4.5)	mol H ⁺ /kg	1.72	0.02	2.50	0.10	3.52	0.20	3.68	0.14

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 CO₂ does not precipitate alkalinity.

Jones et al. [37] used the same red mud for their study, however the data collected in this study disagrees with their data. Jones et al. [37] found that during CO₂ neutralization that 80% of the soluble alkalinity precipitated, whereas this work indicates that little or no alkalinity precipitated during CO₂ neutralization. As this work uses the methodology of Jones et al. [37], the differences seen must be a discrepancy in data reporting. Hence, given that the raw red mud is diluted by a factor of 5:1 to allow a CO₂ to bubble freely and mix in the reaction vessel suggests that Jones et al. [37] have failed to account for the 5 times dilution factor, and thus gain a 80% reduction. A 5 times dilution factor that was not worked back into their results greatly affects some interpretations made by Jones et al. [37] especially that Dawsonite formation is a major control on alkalinity for CO₂-neutralized red muds. Clearly, data here (Table 2) suggests that little or no Dawsonite precipitation occurs in solution. Although Dawsonite is thermodynamically favourable [40] the data presented indicate that Eqs. (8) and (9) are kinetically more favourable than Eqs. (10) or (11). Eq. (11) is a simplification of Eq. (10), because under alkaline conditions H⁺ and HCO₃⁻ cannot exist simultaneously in solution in stoichiometric proportions except under localised micro-gradients and interfaces because:



Most authors suggest that Dawsonite formation, especially in deep alkaline brines, is through a CO₂ and HCO₃⁻ attack of aluminosilicates (e.g. 41). In addition, that this formation is most favourable under elevated pCO₂ conditions [42], whereas the experimental conditions of this work are at relatively low pCO₂ conditions. Furthermore, Hellevang et al. [42,43] state that carbonate minerals such as Siderite (FeCO₃), Calcite (CaCO₃) and Magnesite (MgCO₃) are unlikely to precipitate in preference to Dawsonite only because of the low concentration of these ions in natural waters. Hellevang et al. [42] also notes that the addition of calcium into the system made the Dawsonite formed more stable, though the Ca compete for CO₃ ions and reduce the overall Dawsonite concentration precipitated.

The Alcoa utilises liquid CO₂ to affect a CO₂ neutralization, which would provide much higher pCO₂ conditions, which can generate much higher localised micro-gradient H⁺ concentrations at the CO₂ liquid and red mud brine interface. Hence, the high solubility of Dawsonite at low pCO₂, the temperature, and the short reaction time of 25 min are unlikely to provide suitable geochemical conditions required for Dawsonite formation [41–43]. In addition, Dawsonite precipitation will be affected by the concentration of aluminate in solution and hence the dilution of samples to affect a suitable fluidity for CO₂ addition under low pressure, have probably skewed precipitation to kinetically more favourable Eqs. (8) and (9) rather than Eqs. (10) and (11).

Although carbonation of UNRM converts alkalinity and reduces pH (CNRM), data here indicates alkalinity remains highly soluble and in the surface waters in sodium forms (Table 3). Moreover, although UNRM will draw CO₂ from the atmosphere naturally, this may take several hundreds of years to accomplish fully. In addition, few jurisdictions will allow the discharge of surface waters with alkalinities greater than about 200 mg/L [44], which means that CNRM waters need to evaporate within ponds. This evaporation means that UNRM and CNRM will tend retain high sodium contents, thereby making them less suitable for environmental reuse [44].

Despite the drawbacks of CO₂ neutralization outlined, this study demonstrates the potential to combine several existing methods of red mud neutralization into a hybrid system that consumes

≈17 g CO₂/kg of red mud by the conversion of dissolved NaOH and NaCO₃ to NaHCO₃ before precipitation as Ca- and Mg-CO₃. The CO₂ neutralization used for the Hybrid and CNRM treatments also precipitates soluble Al as Al(OH)₃. The Hybrid neutralized residual liquor can also be more readily discharged than UNRM or CNRM due to the reduction in soluble alkalinity to 300 mg/L CaCO₃, though further work should be conducted to determine if the residual liquor alkalinity can be brought <200 mg/L CaCO₃ by precipitation rather than acid addition. Overall the Hybrid solid is chemically similar to the Basecon™ neutralized solid, suggesting that it can be employed in environmental and industrial applications that Bauxsol™ is current used for. However, the differences in precipitated minerals between the Hybrid and Basecon™ treatments may affect the solubility and environmental longevity of the products, and guide potential applications.

4. Conclusions

This paper demonstrates that there are distinct differences in neutralization techniques and the data show that the neutralization techniques form two distinct geochemical groups when discriminated on total alkalinity alone: those that precipitate alkalinity (Basecon™ and Hybrid) and those that do not (CNRM). All neutralization techniques produce a lower SNL pH and EC, and a lower solid pH and higher solid alkalinity than the un-neutralized red mud. However, each treatment is distinctly different from UNRM and each other, based on the alkalinity speciation (hydroxide-dominant or carbonate/bicarbonate dominant) and residual Ca, Mg and Al in the treatment solution.

The solids produced from each neutralization technique are also different from each other in terms of their reaction pH and ANC, although all treated samples have pHs of around 8.3. The reduction in solid pH to about 8.3 means that the solids will fall outside of the Basel Convention Guidelines, and may, therefore be transported across state borders, thereby increasing the reuse potential. Both the Basecon™ and Hybrid solids had increased ANC compared to CNRM and UNRM, clearly demonstrating increased alkaline precipitation brought about by Ca and Mg additions. A distinct absence of significant alkalinity precipitation in the CNRM treatment is contrary to other studies, where Dawsonite is associated with substantial alkalinity precipitation. This absence is attributed to poor data reporting in the other studies, or because of differences in methodology. However, despite the absence precipitated alkalinity during CNRM neutralization there is approximately 17 g of CO₂/kg of red mud consumed, which is subsequently sequestered by precipitation in the Hybrid neutralization.

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