



Comparison of several different neutralisations to a bauxite refinery residue: Potential effectiveness environmental ameliorants



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ABSTRACT

Bauxite refinery residues (BRR) remain the single largest environmental problem for the alumina industry, because of the fine-grained nature (>90% at <10 μm), high pH (>13), high sodicity (>50 g/kg), and high alkalinity (typically ≈30 g/kg as equivalent CaCO₃). However, neutralisation of BRR provides a geochemically engineered solution, with potential re-use options. Hence, we compare the geochemistry of 4 BRRs: the un-neutralised raw red mud (UNRM), a CO₂-neutralised red mud (CNRM), a Basecon™-neutralised (Basecon™) red mud, and a CO₂-neutralisation followed by a Basecon™-neutralisation (Hybrid) material from a common source for reuse potential. Compositional changes, including acid neutralising capacity, trace-metal and phosphorous binding capacities, and toxicity leaching characteristics (TCLP) show that different neutralisations produce two geochemically distinct solids, those without alkalinity precipitation, and those with solid alkalinity. From the work completed, both Basecon™-neutralised and Hybrid materials have a significantly higher reuse potential for environmental remediation programs, such as acid rock drainage neutralisations, wastewater treatment, and/or artificial soil construction.

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1. Introduction

1.1. Background

Bauxite, produced by intense chemical weathering, contains gibbsite (Al(OH)₃), diaspore (β-AlOOH), boehmite (γ-AlOOH) and hematite (Fe₂O₃), which is digested in a caustic (pH > 12) Bayer process at elevated temperature and pressure to produce two output streams; a liquor pregnant with alumina as aluminate ([Al(OH)₄]⁻) for alumina precipitation, and a solid bauxite refining residue (BRR) or red mud. A BRR slurry has an initial liquor/moisture content ranging from 50–70% that is often reduced to 30–35% by dry stacking, with the liquor re-cycled through the plant after filtration (Bott et al., 2005; Cooling and Jamieson, 2004; Hind et al., 1999). The sheer size of the alumina industry is such that global production estimates for BRR are some 120 million tonnes/year, with a 2007 global inventory of ≈2.7 billion tonnes (Power et al., 2011); between 1.1 and 6.2 tons are produced per tonne of alumina (McConchie et al., 2005). Because of the high caustic content and sodicity, a wide range of trace metal contaminants, high pH (>13), and alkalinity (≈30,000 mg/L as equivalent CaCO₃), BRR represents a major ecological and economic problem worldwide (Hanahan et al., 2004; Hind et al., 1999; Howe et al., 2011; McConchie et al., 2005; Zhang et al., 2001).

Although, considerable research has been conducted on BRRs, and much effort made to reduce or reuse this waste material, the vast majority continues to go to surface impoundments for long-term storage. Moreover, geochemistry of BRR is such that it is listed as a contaminated waste under the Basel Convention (Basal-Convention., 1992), limiting its transportation for storage, disposal or treatment applications, and re-use options (Hanahan et al., 2004; Hind et al., 1999; Howe et al., 2011; Klauber et al., 2011; McConchie et al., 2005; Paramguru et al., 2005; Power et al., 2011; Zhang et al., 2001).

Because of the high alkalinity, BRR has a high acid neutralising capacity (up to 10 M H⁺/kg depending on the source of the BRR, mainly via soluble OH⁻ and CO₃²⁻) (McConchie et al., 2005). Moreover, the fine-grained nature of the solids also provides potential surface sorption sites (Akhurst et al., 2006; Clark et al., 2011b, 2012; Collins et al., 2014; Freire, 2011; Genc-Fuhrman et al., 2005, 2004), hence BRR and some neutralised derivatives have been used to treat acid mine drainage (AMD), acidic sediments and soils, and industrial effluents (Clark et al., 2006; Despland et al., 2011; Munro et al., 2004). In addition, BRR and some neutralised derivatives have successfully been used as a landfill cover, odour reducers, catalysts, road base, fertilizer filler, permeable reactive barriers, as a clay cap, ceramics and glass-ceramic manufacture, geo-polymers, construction materials, and synthetic soils (Barbhuiya et al., 2011a, 2011b, 2010; Despland et al., 2011; Lapointe et al., 2006; Lin et al., 2002; McPharlin et al., 1994; Ordonez et al., 2001; Pan et al., 2003).

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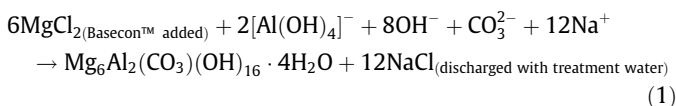
E-mail address: malcolm.clark@scu.edu.au (M.W. Clark).

1.2. Current treatment techniques

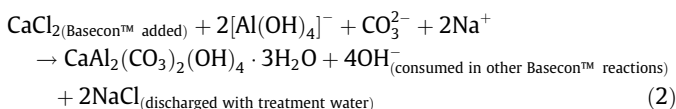
Although many neutralisation techniques have been investigated for BRR, three main neutralisations have the greatest potential to provide sustainable outcomes. These three methods are CO₂-neutralisation a CO₂ gas re-circulation from Alcoa (see, Jones et al., 2006; Nikraz et al., 2007); seawater neutralisation from QAL (see, Hanahan et al., 2004; Menzies et al., 2004); and Basecon™ an engineered and artificial seawater neutralisation from Virotec (McConchie et al., 2001). Each method produces a material that has improved storage, transport and re-use options over the raw BRR.

Seawater neutralisation of BRR involves the addition of excess seawater (up to 20 times the volume of mud) to precipitate the soluble hydroxides and carbonates as insoluble hydroxides (Mg₃(OH)₆), carbonates (CaCO₃ and MgCO₃) and hydroxy-carbonates (Mg₆Al₂(CO₃)(OH)₁₆·4H₂O, CaAl₂(CO₃)₂(OH)₄·3H₂O). However seawater neutralisation is generally only available to processing plants close to oceanic waters, where residual seawater can be discharged back to the ocean (Hanahan et al., 2004; Menzies et al., 2004). The Basecon™ procedure developed (McConchie et al., 2001) utilises high concentration Ca and Mg-rich brines both artificial, natural or enhanced natural brines, where the Ca:Mg ratios may be varied to favour particular mineral precipitates (Despland et al., 2010; McConchie et al., 2001) to produce Bauxsol™ (Basecon™-neutralised red mud). However, too high a proportion of Ca favours hydrocalumite-like mineral formation, which can readily revert (Eqs. (5) and (6); Palmer et al., 2011a, 2011b), where the resulting Ca(OH)₂ rapidly increase pH above the desirable limit of <10 (Basal-Convention., 1992). Hydrotalcite-like minerals (Eq. (1)) may also revert, but the much lower solubility of brucite (Mg(OH)₂) restricts the pH climbing as much as the Ca equivalent materials. Hence, because Basecon™ is regarded as a manufacturing process, Basecon™-neutralised red mud (Bauxsol™) is classified as saleable manufactured product and not a “Green Waste” (Brunori et al., 2005). However, the key chemistry of both Basecon™ and seawater neutralisation are the precipitation of hydrotalcite and para-aluminohydrocalcite (Eqs. (1)–(3)), although other minor reactions of simple carbonates and hydroxides are also possible (Eq. (4)).

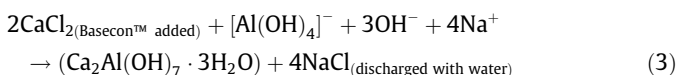
Hydrotalcite



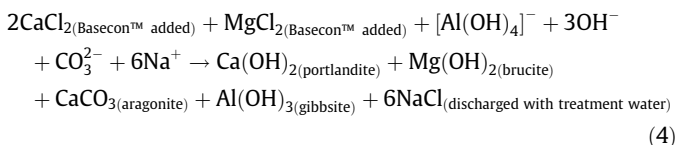
Para-aluminohydrocalcite



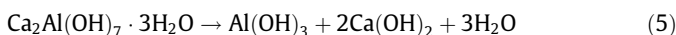
Hydrocalumite



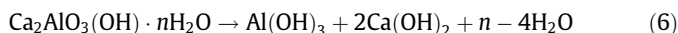
Gibbsite, Aragonite, Portlandite, and Brucite



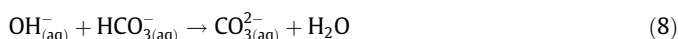
Hydrocalumite Reversion



Hydrated Calcium Aluminate Reversion

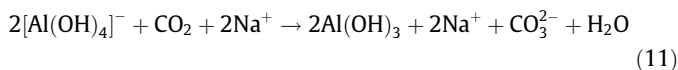
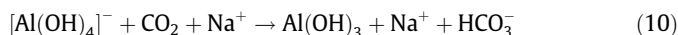


A CO₂-neutralisation utilises the reaction of CO₂ with hydroxide to form bi-carbonate and the reversibility of key alkalinity reactions between hydroxide, carbonate and bicarbonate (Eqs. (7)–(9)). The innovative nature of this neutralisation is the consumption of CO₂ to reduce atmospheric and industrial 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 (pH < 8.5), and consumes CO₂.

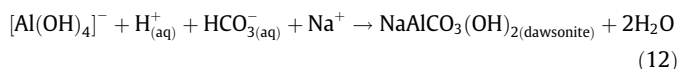


However, red mud liquors are not simple hydroxide solutions as much of the hydroxide is involved in the solubilisation of residual aluminium as aluminate and the consumption of free hydroxide and hydroxide from the aluminate anion causes precipitation of gibbsite (Eqs. (10) and (11)).

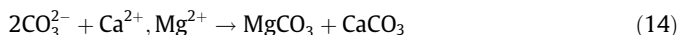
Gibbsite



Consequently, soluble carbonate (CO₃^{2−}) and bi-carbonate (HCO₃[−]) ions should be the dominant products of the CO₂ neutralisation process, without substantially adding to, or reducing total alkalinity of the decant liquor (Freire et al., 2012; Johnston et al., 2010). However, several authors claim that dawsonite precipitation is observed (Cooling et al., 2002; Guilfoyle et al., 2005; Jones et al., 2006) (Eqs. (12) and (13)).



The simple chemistry of Eqs. (10) and (11) suggest that the CO₂ neutralisation method (Johnston et al., 2008) mostly affects the speciation of the alkalinity rather than solubility, hence there is further potential to combine CO₂ neutralisations with a Basecon™ neutralisation (Johnston et al., 2008, 2010). The resulting chemistry does not provide the complex mineral precipitation of a direct Basecon™ neutralisation, but rather a much simpler chemistry of:



allowing for a reduction in soluble alkalinity through carbonate precipitation.

Although, a composite neutralisation has been made previously (Johnston et al., 2008, 2010), only a cursory investigation of the chemistry of the products is made. Since each neutralisation technique outlined has profound effects on the chemistry of the residual solids and liquor, these need to be investigated in depth (Freire et al., 2012; Johnston et al., 2010). We have published previously on the effect that these different neutralisation techniques have on alkalinity solubility, supernatant liquor geochemistry, and toxicology (Howe et al., 2011; Johnston et al., 2010), however no comparison on the effectiveness of these neutralised solids for reuse or as environmental ameliorant has been made. Consequently, neutralisation techniques that do not adequately deal with the toxic

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