

NEW STRATEGIES FOR THE MANAGEMENT OF BAUXITE REFINERY RESIDUES (RED MUD)

McConchie, D., Clark, M., Davies-McConchie, F.

Virotec International Geochemical Research Group, Southern Cross University, East Lismore, NSW, Australia

Abstract

Alumina production results in the creation of large quantities of caustic red mud that must be stored indefinitely or reused; long term storage costs and liabilities are high and reuse usually requires some neutralisation of the caustic material. Of the various alternative red mud neutralisation methods, we find that the most useful involves treatment with seawater or other natural or artificial Ca- and Mg-rich brines to convert the basicity and other soluble alkalinity into low solubility hydroxide, carbonate and hydroxycarbonate minerals. The resulting neutralised red mud is an ideal raw material for the manufacture of commercial reagents to treat acidic and/or metal contaminated waters or sulphidic waste rock, tailings or soils, industrial waste water and sewage effluent.

This paper describes the BASECON™ neutralisation procedure and the geochemical processes involved in red mud neutralisation using Ca- and Mg-rich fluids, and outlines ways to optimise the neutralisation procedure to reduce the quantities of neutralising fluid required and total treatment costs. Optimisation involves the use of a geochemical model to indicate the most cost-effective neutralisation procedure for the red mud; it can also be applied to neutralisation of the supernatant liquor that can be separated from raw red mud by compaction and drainage. The treated red mud is environmentally safe to store or transport and some examples of the market for this material will be presented. After minor additional treatment, the spent neutralising fluid can be safely discharged to the sea or retained in an evaporating basin for salt recovery.

1. Introduction

The production of alumina by the Bayer Process results in the creation of process residues (red mud) that must be stored indefinitely or reused; the production of one ton of alumina usually results in the creation of between one and two dry tons of red mud. Raw red mud is highly caustic (pH is usually > 13.2) and there are substantial problems associated with its storage, including:

- the cost of constructing and maintaining red mud containment facilities is high and the land used for red mud storage is not available for other purposes,
- caustic red mud presents a serious threat to the health of any wildlife or humans that come in contact with it,
- preventing the escape of caustic leachate into groundwater systems, or treating any contaminated groundwater, is difficult and expensive and may need to be continued long after red mud deposition in the storage facility has ceased,
- the costs of public liability insurance, environmental protection and remediation bonds, and completing final rehabilitation work are high and are likely to increase in the future, and
- the costs of managing and maintaining caustic red mud storage facilities are high.

These costs and liabilities can best be reduced by not having to store the red mud, but not having to store it requires that it is reused in some application and both transport and reuse will usually require at least partial neutralisation of the caustic component of the red mud. Natural weathering processes will eventually neutralise stored red mud, but adequate neutralisation will take many decades to achieve and in the interim all the problems listed above will be applicable. Thus, it is desirable to neutralise the red mud in such a way that it is no longer highly caustic and several alternative procedures for achieving this objective have been tried, including:

- A. Adding acids (usually waste sulphuric acid or acidic water produced when scrubbers are used to remove acid forming gasses from industrial emissions such as those resulting from coal combustion) to reduce the pH below 10.5 for safer storage.
- B. Adding large volumes of seawater, or evaporatively concentrated seawater, or calcium- and magnesium-rich brines, or soluble calcium and magnesium salts (usually calcium and magnesium chloride), or some combination of these alternatives to convert the basicity (mainly sodium hydroxide) and other soluble alkalinity (mainly sodium carbonate) into low solubility compounds (particularly: aragonite, brucite, calcite, hydrocalumite, hydrotalcite and p-aluminohydrocalcite); sodium released in the process can be discharged.
- C. Using a caustic red mud suspension as a scrubbing agent to neutralise acid forming gasses produced during coal combustion or similar processes.
- D. Adding gypsum and/or treating the wet red mud with large volumes of carbon dioxide. There are also other options, but none are in widespread use.

All of these strategies can be used with varying degrees of efficiency to neutralise the caustic red mud and thereby wholly or partly resolve some of the red mud storage and management problems listed above. However, with the exception of reprocessing to recover other elements such as titanium, most high volume reuse options that would solve all the red mud storage and management problems, make use of the intrinsic ability of the red mud to neutralise acid and to trap and bind a wide range of trace metals and other inorganic substances and this requirement imposes serious constraints on the selection of neutralisation options. Limitations on the alternative neutralisation options listed above can be summarised as follows:

- A) This technique is reasonably cheap if sufficient (large) quantities of waste acid are available and need to be disposed of and is particularly applicable where

contaminated waste acids are produced during scrubbing of acid forming gasses (primarily sulphur dioxide) produced during coal combustion or other industrial processes such as sulphide mineral roasting. However, sufficient quantities of acid to neutralise all the red mud are seldom available near an alumina refinery and, more critically, the resulting neutralised red mud has almost no value for reuse in treating acidic and/or metal contaminated waters or sulphidic waste rock, tailings or soils. Thus, unless some new reuse for this material is identified, red mud neutralised in this way must be stored indefinitely and the storage area must ultimately be rehabilitated.

B) The use of seawater can be very effective for refineries that are near the coast and the process can be made more efficient if the site is in an arid or semi-arid area where evaporatively concentrated seawater is available; the addition of seawater to facilitate red mud pumping will also help conserve fresh water (e.g. Graham and Fawkes, 1992). However, large amounts of seawater will be required (typically between 12 and 18 times the volume of red mud to be neutralised) if the discharge water is to meet normal environmental standards and large ponds will be required to allow the solids to settle before the calcium and magnesium depleted seawater used in the neutralisation process can be returned to the sea. These limitations add substantially to the cost of the neutralisation process.

The use of natural calcium- and magnesium-rich groundwater or salt lake brines may be an effective option for refineries that are not close to the coast, but suitable brines would need to be available (in arid or semi-arid areas brines could also be concentrated in a large evaporating basin before use). Evaporating basins would also be necessary for holding the sodium-enriched and calcium- and magnesium-depleted brines remaining after use in the red mud neutralisation process, but the cost of these could be offset by the production of some high quality salts from the residual brines.

The option of adding soluble calcium and magnesium salts (usually the chloride salts) to water used to neutralise the red mud, has benefits for refineries that are remote from the coast, but large quantities of the salts may be required and hence, even allowing for the use of low purity salts, the cost would be very high. Thus, the use of calcium and magnesium salts alone to neutralise the red mud is not a viable option, but the addition of some calcium and magnesium salts to seawater, or to evaporatively concentrated seawater, or to other saline brines being used to neutralise red mud, can substantially reduce brine volumes required and can be shown to result in cost savings that exceed the cost of the added salts.

The neutralised red mud produced by any of these processes is highly suitable for reuse as a raw material in the production of commercial reagents to treat acidic and/or metal contaminated waters or sulphidic waste rock, tailings or soils, etc. The neutralised red mud is also safe to store and fairly easy to rehabilitate and consequently, whether it is reused or not, the long term management costs are substantially reduced.

C) The technique of using suspensions of the caustic red mud as a scrubbing agent to neutralise acid forming gasses in industrial emissions (e.g. from coal combustion or sulphide mineral roasting facilities) can be very effective, but its primary purpose is cleaning the gas emissions and not neutralising the red mud. Neutralising the red mud is an incidental benefit and the resulting neutralised red mud has almost no value for reuse in treating acidic and/or metal contaminated waters or sulphidic waste rock, tailings or soils; unless some new reuse for this material is identified, it must be stored indefinitely and the storage area must ultimately be rehabilitated.

D) Neutralisation using gypsum or carbon dioxide or similar strategies can produce a red mud that is safe to store. However, the procedures can be costly and the resulting neutralised red mud has almost no value for reuse in treating acidic and/or metal contaminated waters or sulphidic waste rock, tailings or soils and unless some new reuse for this material is identified, it must be stored indefinitely and the storage area must ultimately be rehabilitated.

Essentially, if red mud is to be neutralised to allow safe storage, there are several alternative neutralisation techniques that could be used, but the only treatment strategy that will currently facilitate the reuse of large volumes of neutralised red mud is the method that involves the use of seawater or concentrated seawater, or other calcium- and magnesium-rich brines, or a mixture of soluble calcium and magnesium salts (usually the chloride salts), or some combination of these alternatives.

There is now a well established need for appropriately neutralised red mud that can be used as the starting material to produce a range of marketable environmental management and remediation products (e.g. ViroSewage™ and ViroMine™ reagents developed from Bauxsol Technology™) and all available information suggests that environmental management and remediation products provide the best currently available option for reusing large volumes of red mud. Potentially, these products could consume all the red mud that is produced and the red mud that is currently stored in containment ponds.

Commercial estimates confirm that large quantities of neutralised red mud will be required as the base ingredient in the manufacture of environmental products. For example, it is estimated that within 5 years in excess of 1 million tonnes may be required annually in the US, just to produce ViroSewage reagents for use in sewage treatment facilities.

Although harder to quantify, independent reports commissioned by Virotec suggest the potential annual use of neutralised red mud in the production and manufacture of their ViroMine™ reagents could exceed 19 million tons per year within 20 years. Similar or greater quantities could also be used in treating sulphidic waste rock, mine tailings and or acid sulphate soils.

Commercial products developed from Bauxsol Technology™ using neutralised red mud, not only have an outstanding ability to bind metals in non-bioavailable forms; in many applications they outperform lime based products environmentally and technically. Unlike lime, they are not water soluble and cannot be leached from soil by rainwater or groundwater; consequently they will remain in place without losing their acid neutralising capacity and remain stable for long periods of time i.e. 20 years.

The biggest problem may well be that the demand for suitably neutralised red mud will exceed supply in the near future (Virotec marketing division, pers. comm.)

Consequently, the greatest need may not be to determine how best to store or dispose of red mud, but how to make suitably neutralised red mud quickly and as cheaply as possible. Thus, the main focus of this paper is on how to make suitably neutralised red mud in the most cost-effective manner, whether it is to be reused immediately or stored for use in the future.

2. Basecon™ — The Preferred Neutralisation Procedure

Accepting that reuse of neutralised red mud is a better option than storing it indefinitely, then the only neutralisation procedures that can be considered are those that involve the conversion of basicity (mainly sodium hydroxide) and soluble alkalinity (mainly sodium carbonate) into alkalinity

that is retained as solid hydroxide, carbonate or hydroxycarbonate minerals. Furthermore, as a consequence of the increasing international demand for products developed from Bauxsol Technology™, Virotec has strong interest in developing cheaper and faster methods for producing suitably neutralised red mud that can be used as the raw material to manufacture many of its patented environmental reagents. With these objectives in mind, the authors have developed the BASECON™ process, described below and patented by Virotec, which offers the most cost-effective method that we currently know of to neutralise red mud in such a way that it remains suitable for reuse in many environmental applications.

When seawater, or evaporatively concentrated seawater, or other Ca- and Mg-rich brines (e.g. groundwater or salt lake brines or some industrial wastewaters), or a mixture of soluble Ca and Mg salts (usually the chloride salts), or any combination of these alternatives, is added to the caustic red mud, or to the supernatant liquor that can be separated from the caustic red mud, the pH of the mixture is reduced and hydroxide, carbonate or hydroxycarbonate minerals are precipitated. The neutralising effect of the calcium and magnesium ions is initially large but decreases rapidly as complete neutralisation is approached. Neutralisation is considered to be complete when the liquid that can be separated from the treated red mud/treating solution mixture has a pH less than 9.0 and a total alkalinity less than 200 mg/L (as calcium carbonate equivalent alkalinity); such water can be safely discharged to the marine environment.

Examination of red muds supplied by several refineries in Australia, Europe, North America and South America shows that complete neutralisation using seawater alone can require the addition of between 10 and 20 volumes of world average seawater (412 mg Ca/L and 1,290 mg Mg/L; Krauskopf and Bird, 1995) for each volume of red mud waste or similar quantities of Ca and Mg supplied by other means. The exact amount of seawater required will depend on the proportion of solids in the original red mud and on its initial alkalinity and on the Ca and Mg concentrations in the locally available seawater. Such complete neutralisation requires a lot of seawater and therefore involves high pumping, water storage and water management costs, but slightly less complete neutralisation can be achieved using much less seawater. For example, if an untreated red mud has a pH of about 13.5 and an alkalinity of about 20,000 mg/L, the addition of about 5 volumes of world average seawater will reduce the pH to between 9.0 and 9.5 and the alkalinity to about 300 mg/L. However, the addition of a further 8 to 12 volumes of world average seawater will be required to reduce the pH to below 9.0 and the alkalinity to less than 200 mg/L as required for water to be discharged to the marine environment. If the original alkalinity of the red mud is higher or lower than the example value of about 20,000 mg/L, then the amount of seawater required for partial or complete treatment would need to be increased or decreased in direct proportion to the increase or decrease in the alkalinity above or below the 20,000 mg/L value. What this means is that greater than 95% of the neutralising treatment can be completed using about one third of the amount of seawater required for complete treatment, thereby resulting in substantially reduced water handling and storage costs. To optimise treatment, the solid and liquid fractions should be thoroughly mixed and kept in contact for at least 30 mins.

In the next step, the largely neutralised solid material is separated from the liquid fraction by settling. The resulting solids will comply with the regulatory requirements for safe transport and reuse in a wide range of applications, but

the liquid fraction will need additional treatment before it will comply with the requirements for discharge to the marine environment. At this stage the liquid fraction will have a pH of between 9.0 and 9.5, which will need to be reduced to less than 9.0, and it will have an alkalinity of about 300 mg/L, which will need to be reduced to 200 mg/L or less. Once the liquid fraction is separated from the solid fraction, reduction of the pH and the alkalinity of the liquid fraction can readily be achieved by adding a small quantity of acid (waste acid or acidic water from scrubbers in gas emission stacks is ideal). The amount of acid required, however, is not nearly as great as would be required to neutralise the original red mud; for example, if about 400 moles of acid (roughly 11 L of conc. sulphuric acid) would be needed to neutralise 1 kL of the original red mud to discharge standards, only 2 moles (roughly 0.05 L of conc. sulphuric acid) are required to neutralise 1 kL of the separated liquid after treatment with seawater as described above. It is therefore clear that adding a small amount of acid to the original red mud will have a negligible effect on neutralising the red mud whereas adding the same amount of acid to the liquid remaining after seawater treatment of the red mud and removal of the solid fraction will have a very large effect on final water quality. It is also important to note that if the solid and liquid fractions are not separated after seawater treatment, then the amount of acid that will be required to reduce the pH to below 9.0 and the alkalinity to below 200 mg/L will be similar to the amount that would be required to neutralise red mud that had not been treated with any seawater.

The procedure described above can also be used in the neutralisation of any supernatant caustic liquor that may be separated from the red mud before any red mud treatment is commenced or at any stage of partial treatment of the red mud.

The liquid remaining after seawater treatment, separation of the solid and liquid phases, and addition of some acid to reduce the pH to below 9.0 and the alkalinity to below 200 mg/L, will be depleted in calcium and magnesium and enriched in sodium relative to the brine originally added to the red mud. The concentration of some trace metals in the liquid may also be reduced relative to concentrations in the brine originally added to the red mud (c.f. McConchie et al., 1996). This residual liquid will be of acceptable quality for discharge to the marine environment or to the more saline parts of estuaries (c.f. ANZECC, 1992). In practice, the addition of the acid to the discharge water can be automated to achieve any desired target pH value.

In circumstances where the brines remaining after red mud neutralisation and solids separation are not to be discharged (e.g. at refineries that are not near the sea), it may be neither necessary nor desirable to add any acid because it will not be necessary to reduce the pH to below 9.0 and the alkalinity to below 200 mg/L. In these situations it may be desirable to keep the Na-enriched and Ca- and Mg-depleted brines as pure as possible so that they can be used for the controlled precipitation of marketable salts; research on the chemical and physical manipulation of these brines to produce marketable salts is currently in progress.

3. How the Neutralisation Works

Neutralisation is achieved when seawater or evaporatively concentrated seawater, or other Ca- and Mg-rich brines, or a mixture of soluble Ca and Mg salts (usually the chloride salts), or any combination of these alternatives is added to the red mud by converting soluble hydroxides and carbonates into low solubility mineral precipitates (McConchie et al., 2000b). This procedure lowers the basicity to a pH of about 9.0 and converts most of the

soluble alkalinity into solid alkalinity. More specifically, hydroxyl ions in the red mud wastes are largely neutralised by reaction with magnesium in the seawater to form brucite $[\text{Mg}_3(\text{OH})_6]$ and hydrotalcite $[\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}]$, but some are also consumed in the precipitation of additional boehmite $[\text{AlOOH}]$ and gibbsite $[\text{Al}(\text{OH})_3]$ and some reacts with calcium in the seawater to form hydrocalumite $[\text{Ca}_2\text{Al}(\text{OH})_7\cdot 3\text{H}_2\text{O}]$ and p-aluminohydrocalcite $[\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4\cdot 3\text{H}_2\text{O}]$. Most of the boehmite and gibbsite is present in the red mud wastes before the seawater is added, but crystal growth continues as the pH of the mixture decreases and aluminium becomes less soluble. Simultaneously, calcium in the seawater reduces the carbonate alkalinity in the red mud wastes by forming calcite and/or aragonite $[\text{CaCO}_3]$; some carbonate may also be removed during the formation of hydrotalcite and p-aluminohydrocalcite (carbonate ions can isomorphously substitute for hydroxyl ions in these minerals). Some Ca may also be consumed in the formation of other minerals such as whewellite (at refineries that add the oxalate waste stream into the red mud waste stream) and fluorite (where the fluoride concentration in the red mud waste stream is greater than about 4 mg/L) and some Mg may be consumed where it isomorphously substitutes for Ca in aragonite.

When neutralising the red mud, both "base amounts" and "treating amounts" of Ca and Mg are required. The treating amounts of Mg and Ca take part in the reactions described above and are amounts over and above the base amounts, which represent the concentrations below which minimal treatment will occur. The base amounts also represent the minimum amounts that are likely to be present in solution once at least 50% of the neutralisation has been completed; i.e. not all the Ca and Mg will react. For treatment of the red mud to a pH of 9.0–9.5 and an alkalinity of about 300 mg/L as described in the previous section, the base amount for Ca is about 150 mg/L (about 4 millimoles/L) and the base amount for Mg is about 250 mg/L (about 10 millimoles/L) and unless the Ca and Mg concentrations are in excess of these amounts, neutralisation reactions will proceed extremely slowly if at all. For treatment to a final pH of less than 9.0 and an alkalinity of less than 200 mg/L, the base amounts for Ca and Mg are slightly higher at about 180 mg/L and 320 mg/L respectively; the base amounts of Ca and Mg required increase as the pH and alkalinity of the treated red mud approach those of the seawater being used to effect neutralisation.

It has also been found that for efficient neutralisation, the amount of Ca and Mg present in the treating solution should be not less than 300 mg/L for Ca (about 7.5 millimoles/L) and 750 mg/L for Mg (about 30 millimoles/L); this amount is equivalent to the base amount of Ca plus 150 mg/L Ca and the base amount of Mg plus 500 mg/L Mg. Reactions using lesser amounts of Ca and/or Mg will be slow and will involve undesirably large volumes of treating fluids. Conversely, greater concentrations will work much more efficiently and will involve greatly reduced treating fluid volumes. For red mud with an initial alkalinity of 20,000 mg/L treating amounts of about 4,200 mg of magnesium and 1,000 mg of calcium will be required per litre of the red mud; more would be required for red mud with a higher initial alkalinity and less for red mud with a lower initial alkalinity. Ideally, the ratio of the treating amount of magnesium to the treating amount of calcium should be about 14 moles of Mg per mole of Ca (i.e. 8.4 g Mg : 1 g Ca), but variation in the molar ratio from about 10 moles of Mg per mole of Ca to about 20 moles of Mg per mole of Ca is acceptable provided that the minimum base amounts and the minimum treating amounts of both Ca and Mg are present.

4. Alternatives to Using Seawater

Seawater is used in the red mud neutralisation procedure primarily as a source of Ca and Mg and therefore, evaporatively concentrated seawater will work more effectively because there is more Ca and Mg present (as the treating amount) over and above the base amounts required. This means that seawater with twice the normal concentration of Ca and Mg is more effective as a neutraliser than twice the volume of normal seawater. Furthermore, because the Mg is more important than the Ca in the neutralisation process, it is possible to use seawater or other brines that are concentrated beyond the point at which calcium carbonate (or even gypsum) can begin to precipitate. Thus, where evaporatively concentrated seawater is available, the volumes of water required to achieve the required degree of neutralisation can be reduced substantially compared to the volumes of normal seawater that would be needed. For example, at twice normal marine salinity, the red mud with an initial alkalinity of about 20,000 mg/L could be adequately neutralised using a little more than 2 kL of the water per 1 kL of the red mud compared to about 5 kL of normal seawater per 1 kL of the red mud. Similarly, if seawater with 1.5 times normal marine salinity is used, red mud with an initial alkalinity of about 20,000 mg/L could be adequately neutralised using about 3.5 kL of the water per 1 kL of the red mud compared to about 5 kL of normal seawater per 1 kL of the red mud.

Where seawater is not available, any other convenient source of Ca- and Mg-rich brines could be used instead to achieve neutralisation. Such brines could be available from natural sources such as hard groundwaters or salt lake brines or they could be available as industrial waste waters, or they could be prepared artificially by adding Ca and Mg salts to brines (including seawater) or to waters that had insufficient Ca and/or Mg. When Ca and Mg salts are added, it is desirable to use the chloride salts which are reasonably cheap and readily available; high purity salts are not necessary. Magnesium sulphate salts could be used, but the solubility of Ca sulphate is too low to work efficiently. Oxides, hydroxides and carbonates of Ca and Mg are not suitable because they will not help reduce the soluble alkalinity.

Where evaporatively concentrated seawater or Ca- and Mg-rich brines, or a mixture of soluble Ca and Mg salts, or any combination of these alternatives is used instead of seawater, red mud neutralisation and discharge water conditioning should follow the same procedure as described above for neutralisation using seawater. However, when using treating solutions that do not include seawater, or evaporatively concentrated seawater, or compositionally similar brines, a reduction in the buffering capacity that is normally supplied by the seawater may mean that pH readings are unstable and may change rapidly. In these circumstances, monitoring the progress of neutralisation should be based on changes in alkalinity and getting the alkalinity down to 300 mg/L or less for the preparation of Bauxsol Technology™ raw material and down to 200 mg/L or less for the preparation of waste water for discharge.

5. Modelling the Neutralisation Process

Detailed examination of red muds from many refineries has enabled the development of a geochemical model that allows rapid calculation of neutralisation requirements for any initial red mud alkalinity and solids content and using any of the various alternative neutralisation procedures. Furthermore, if local labour costs, pumping costs, infrastructure depreciation and maintenance costs, etc. are available, the model can also estimate the costs of neutralisation by any of the alternative neutralisation procedures.

Table 1 — Extract from the BASECON™ neutralisation model showing Ca and Mg requirements for neutralising 1 kL of red mud, with an initial alkalinity of 30,000 g/kL, to a pH of about 9.2 and an alkalinity of about 300 mg/L using seawater and evaporatively concentrated seawater

<i>Run using world average seawater</i>								
kL seawater added	1	2	3	4	5	6	7	8
Base amount Ca needed (kg)	0.30	0.45	0.60	0.75	0.90	1.05	1.20	1.35
Base amount Mg required (kg)	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25
Treating amount of Ca required (kg)	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Treating amount of Mg required (kg)	6.30	6.30	6.30	6.30	6.30	6.30	6.30	6.30
Total Ca required (kg)	1.80	1.95	2.10	2.25	2.40	2.55	2.70	2.85
Total Mg required (kg)	6.80	7.05	7.30	7.55	7.80	8.05	8.30	8.55
Ca available from seawater (kg)	0.41	0.82	1.24	1.65	2.06	2.47	2.88	3.30
Mg available from seawater (kg)	1.29	2.58	3.87	5.16	6.45	7.74	9.03	10.32
Additional CaCl ₂ ·2H ₂ O required (kg)	5.10	4.14	3.18	2.21	1.25	0.29	0.00	0.00
Additional MgCl ₂ ·6H ₂ O required (kg)	46.61	37.81	29.01	20.22	11.42	2.62	0.00	0.00
<i>Run using 1.5 times concentrated world average seawater</i>								
kL seawater added	1	2	3	4	5	6	7	8
Base amount Ca required (kg)	0.30	0.45	0.60	0.75	0.90	1.05	1.20	1.35
Base amount Mg required (kg)	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.25
Treating amount of Ca required (kg)	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Treating amount of Mg required (kg)	6.30	6.30	6.30	6.30	6.30	6.30	6.30	6.30
Total Ca required (kg)	1.80	1.95	2.10	2.25	2.40	2.55	2.70	2.85
Total Mg required (kg)	6.80	7.05	7.30	7.55	7.80	8.05	8.30	8.55
Ca available from seawater (kg)	0.62	1.24	1.85	2.47	3.09	3.71	4.33	4.94
Mg available from seawater (kg)	1.94	3.87	5.81	7.74	9.68	11.61	13.55	15.48
Additional CaCl ₂ ·2H ₂ O required (kg)	4.34	2.62	0.90	0.00	0.00	0.00	0.00	0.00
Additional MgCl ₂ ·6H ₂ O required (kg)	41.15	26.90	12.65	0.00	0.00	0.00	0.00	0.00

Table 1 shows a partial model output for neutralisation using seawater and evaporatively concentrated seawater to treat red mud with an initial alkalinity of 30,000 mg/L (calcium carbonate equivalent alkalinity) to a pH of about 9.2 and an alkalinity of about 300 mg/L. Even this small extract from the model clearly illustrates the benefits of using evaporatively concentrated seawater with the amount of seawater required to achieve neutralisation to the target values decreasing from a little over 6 kL world average seawater per kL of red mud with a 40% solids content to about 3.5 kL of 1.5 times concentrated seawater per kL of red mud.

The model can also be applied to the neutralisation of the supernatant liquor that can be separated from the raw red mud by compaction and drainage.

6. Properties of the neutralised red mud

The partly neutralised red mud produced as described above will consist of a cocktail of very fine grained minerals that usually includes: abundant hematite, boehmite, gibbsite, sodalite, quartz and cancrinite, minor aragonite, brucite, calcite, diaspore, ferrihydrite, gypsum, hydrocalumite, hydrotalcite, lepidocrocite, p-aluminohydrocalcite, portlandite and titanium oxides, and possibly a few low solubility trace minerals (McConchie et al., 1999, 2000b). The exact composition depends on the composition of the bauxite used at each refinery, operational procedures at the refinery and how the caustic red mud is neutralised, but none of the minerals in the mixture are known to be environmentally hazardous. Geotechnically, the mixture of minerals will have a plastic limit at between 30% and 35% moisture, a liquid limit at between 50% and 55% moisture and a linear drying shrinkage of 6–8%. Although the mineral particles are very fine grained (about 80% usually have a particle size of less than 10 microns), the mixture is non-dispersive in water.

Irrespective of its exact composition, the mineral mixture has a high acid neutralising capacity (up to 7.5 moles of acid/kg) and it is now being used as the raw material base of commercial reagents with acid neutralising capacities in excess of 15 moles of acid/kg. Partly neutralised red mud

also has a very high trace metal trapping capacity (greater than 1000 milliequivalents of metal/kg) and as such, it is now being used as the base of commercial reagents with metal trapping capacities in excess of 2000 milliequivalents of metal/kg. It also has a high capacity to trap and bind phosphate and some other chemical species and is an excellent flocculant and commercial reagents being developed as a result of these characteristics will have widespread applications in the sewage treatment industry.

Table 2 — TCLP (Toxicity Characteristic Leaching Procedure) data for BASECON™ neutralised red mud

Contaminant	TCLP value (mg/L)	Threshold value (mg/L)
Arsenic	<0.01	0.5
Beryllium	<0.01	0.1
Cadmium	<0.01	0.1
Chromium (total)	0.036	0.5
Copper	<0.01	No limit set
Lead	<0.01	0.5
Mercury	<0.01	0.02
Molybdenum	<0.01	0.5
Nickel	0.012	0.2
Selenium	<0.02	0.1
Silver	<0.01	0.5
Vanadium	0.06	No limit set
Zinc	<0.01	No limit set

Note: Threshold values are for classification as an inert solid in New South Wales, Australia.

The soil reaction pH of the partly neutralised red mud is sufficiently low and the TCLP (Toxicity Characteristic Leaching Procedure) values (Table 2) for the mineral mixture are sufficiently low that it can be transported and used without the need to obtain permits that are usually required for the transport of potentially hazardous materials; it is safe for unskilled workers to handle.

Consequently, the partly neutralised red mud is an excellent raw material for preparing the various environmental management and remediation reagents required for the

Bauxsol Technology™. (e.g. Table 3; see also McConchie et al., 1999, 2000b)

Equally importantly, the metals that are bound when the material is used to treat contaminated water are held very tightly and only a small proportion can be released even if the solid residue is leached at a pH of 2.88. Furthermore, the longer the residue is left to age after use, the more tightly the metals are held and as the residue ages some new metal trapping capacity develops; for example, if the residue is left in a tailings dam or pit lake after the completion of treatment, the metal concentrations in the water will continue to decrease for at least twelve months.

Table 3 — Effect of treating water from Captains Flat, New South Wales with Bauxsol Technology™ reagents, by direct addition methods and by passing it through a permeable reactive barrier (PRB)

Component	Before treatment	After direct addition	Using a PRB
pH	2.8	8.2	8.4
Aluminium	12,340 µg/L	4.8 µg/L	3.1 µg/L
Cadmium	94 µg/L	0.3 µg/L	0.2 µg/L
Copper	314 µg/L	4.4 µg/L	1.3 µg/L
Iron	38,120 µg/L	0.9 µg/L	0.8 µg/L
Manganese	10,000 µg/L	1,027 µg/L	31 µg/L
Nickel	60 µg/L	22 µg/L	1.4 µg/L
Zinc	122,400 µg/L	18 µg/L	6.3 µg/L

7. Conclusions

The findings of this study show that it is possible to produce a neutralised red mud that is suitable for reuse as a raw material in a wide range of commercial applications using cost-effective neutralisation procedures. Neutralisation of red mud using Virotec's BASECON™ process outlined herein will also reduce both the costs and the risks associated with the long term storage of unneutralised red mud. This neutralisation process is summarised as follows. Step 1: Take the caustic red mud and add seawater (or concentrated seawater, or other calcium- and magnesium-rich brines, or a mixture of soluble calcium and magnesium salts {usually the chloride salts}, or any combination thereof) until the liquid

phase has a pH of 9.0 to 9.5 and an alkalinity of 300 mg/L or less. To optimise treatment, the solid and liquid fractions should be thoroughly mixed and kept in contact for at least 30 mins.

- Step 2: Separate the solid and liquid fractions by settling and decant off the liquid fraction.
- Step 3: Add acid (waste acid or acidic water from scrubbers in gas emission stacks is ideal) to the liquid fraction until the pH is less than 9.0 and the alkalinity is less than 200 mg/L.
- Step 4: Discharge the liquid fraction to the sea or transfer it to an evaporating pond for salt recovery.
- Step 5: Wholly or partly dry the solid fraction, or retain it as a slurry, for reuse or storage as required. The solid material can be further modified by washing with fresh water or by the addition of chemical additives as required for any particular intended reuse.

Although not fully neutralised, the solid fraction is neutralised to well below the strictest standards imposed for safe transport and reuse, which require a reaction pH of less than 10.5 and impose no limits on alkalinity. TCLP (Toxicity Characteristic Leaching Procedure) values for the solid material are sufficiently low that it can be classified as an environmentally safe inert solid. This material can be transported as a slurry or as a dried or partly dried solid for reuse, whichever form is most convenient. If required, the solid material can be further modified by washing with fresh water to remove soluble salts (the wash water can be added to the treatment water produced at Step 3) or by the addition of chemical additives as required for any particular intended reuse.

The BASECON™ procedure outlined here offers the most cost-effective procedure currently known to the authors for neutralising caustic red mud residues from bauxite refineries, such that the treated red mud residues are environmentally safe to store, transport or reuse as the raw material base for a wide range of commercial reagents and such that the residual treatment liquid can be safely discharged to the marine environment or retained in an evaporating basin for salt recovery.

References

- ANZECC, 1992. *Australian Water Quality Guidelines for Fresh and Marine Waters*. Australian and New Zealand Environment and Conservation Council, Australia.
- Graham, G.A. and Fawkes, R., 1992. Red mud disposal management at QAL. *Proc. International Bauxite Tailings Workshop, Perth, 1992*, 188–195.
- Krauskopf, K.B. and Bird, D.K., 1995. *Introduction to Geochemistry* (3rd. Edn.). McGraw-Hill, N.Y.
- McConchie, D. and Clark, M.W., 1996. An Innovative Neutralising Treatment for Acid Sulfate Soils. In: R.J. Smith and H.J. Smith (eds.) *Proceedings of the 2nd National Conference on Acid Sulfate Soils*, Coffs Harbour, September, 1996, R.J. Smith and Associates and ASSMAC Pub., 227–229.
- McConchie, D., Saenger, P. and Fawkes, R., 1996. An environmental assessment of the use of seawater to neutralise bauxite refinery wastes. In: V. Ramachandran and C.C. Nesbitt (eds.) *Proceedings of the 2nd Internat. Symp. on Extraction and Processing for the Treatment and Minimisation of Wastes*, The Minerals, Metals and Materials Soc., Scottsdale, Arizona, Oct., 1996, 407–416.
- McConchie, D., Clark, M., Hanahan, C. and Fawkes, R., 1999. The use of seawater-neutralised bauxite refinery residues (red mud) in environmental remediation programs. In: I. Gaballah, J. Hager and R. Solozabal (eds.) *Proceedings of the 1999 Global Symposium on Recycling, Waste Treatment and Clean Technology*, San Sebastian, Spain. The Minerals, Metals and Materials Society, 1: 391–400.
- McConchie, D. and Clark, M., 2000a. Acid sulphate soil neutralisation techniques. In: P.G. Slavich (ed.) *Proceedings of the Workshop on Remediation and Assessment of Broadacre Acid Sulfate Soils*, held at Southern Cross University, Lismore, 31 August–2 September 1999. Acid Sulphate Soil Management Advisory Committee (ASSMAC), Australia, 88–93. ISBN 0 7347 1209 X.
- McConchie, D., Clark, M., Hanahan, C. and Davies-McConchie, F., 2000b. The use of seawater-neutralised bauxite refinery residues in the management of acid sulphate soils, sulphidic mine tailings and acid mine drainage. In: K. Gaul (ed.) *Proceedings of the 3rd Queensland Environment Conference*, May, 2000, Environmental Engineering Society, 201–208.
- Ward, N.J., Sullivan, L.A., Bush, R.T., McConchie, D.M., and Clark, M., 2000. The neutralising value of CaCO₃ and seawater-neutralised bauxite refinery residue (red mud) for treating acid sulfate soils. In: J.A. Adams and A.K. Metherell, (eds.) *Soil 2000: New Horizons for a New Century*. Australian and New Zealand Joint Soils Conference, New Zealand Society of Soil Science, 3–8 December 2000, Lincoln University, V2: 331–332.