THE DEVELOPMENT OF POROUS PELLETS OF SEAWATER-NEUTRALISED BAUXITE REFINERY RESIDUES (RED MUD) AND BAUXSOL™ FOR USE IN WATER TREATMENT SYSTEMS

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Abstract

Over recent years seawater-neutralised bauxite refinery residues and Bauxsol™ have attracted increased interest for the treatment of waste waters because they have a high acid neutralising capacity and an exceptional capacity to bind heavy metals in environmentally stable forms. However, bauxite refinery residues are typically fine grained (>85% of the residual material is <10μm), and because of their low hydraulic conductivity waste water treatment applications have been limited to a direct addition of dispersed Bauxsol™ to a standing water body. Although dilution with sand to increase hydraulic conductivity is possible, the ratio of active to inert material becomes quite low (<0.35) and the size of the treatment filter increases. Consequently, there is a need to develop a composite material that maintains the high reactive surface area of the iron oxy-hydroxides for metal removal, maintains, or improves the acid neutralising capacity, and increases the active to inert material ratio (ideally >0.65), but also increases the hydraulic conductivity so that fluids may readily pass through the treatment filter.

In this paper we describe a method that allows for the development of a porous pellet using seawater-neutralised bauxite refinery residues and Bauxsol™ that provides the desired properties. Although un-neutralised red mud was also tested, the high residual Na content of this mud results in pellets with extremely poor physical strength properties, and relatively poor geochemical characteristics. This paper also describes some of the physical and geochemical characteristics of the Bauxsol™ based pellets.

1 Introduction

Since 1999 seawater-neutralised red mud and Bauxsol™ have been promoted for the treatment of waste waters, acid rock drainage and industrial effluents because they have an acid neutralising capacity from 2.5–6 M/kg, have exceedingly high metal binding capacities, and also exhibit excellent phosphate and arsenate removal capacities (Clark et al., 2003; 2004; Hanahan, 2001; McConchie et al., 1996; 1999; 2000a,b; 2001; 2003). Bauxsol™ is a manufactured derivative of red mud where the alkalinity of the red mud is converted from soluble to solid by adding Ca and Mg salts, either as solids or as brines, where the ratio and concentrations of Ca:Mg can be manipulated to control mineral precipitates to effect a more efficient conversion of the alkalinity (McConchie et al., 2003). Seawater-neutralised red mud where the alkalinity of the red mud has been converted from soluble to solid using a typical seawater where Mg concentrations are about 1200mg/L and Ca concentrations are about 400mg/L. The geochemical behaviour of the two materials are virtually identical when applied to metal-rich effluents, such that performance is typically <5% the margin of error for geochemical analyses. It was noted very early on in the application of these materials that when used as a filter cake rather than just added as a dry powder directly to the water, that better metal removal efficiencies could be achieved (McConchie et al., 1996; 1999; 2000a,b; 2001; 2003). Although the treatment of the metals is much better when using the materials as a filter cake, the quantity of water that can be passed through the filter is low, because of the fine grained nature of the Bauxsol™, the hydraulic conductivity of the filter is very low <1 × 10^{-6} cm/sec. However, this low hydraulic conductivity can be overcome by blending the fine grained reactive Bauxsol™ with a coarse grained inert solid (e.g. sand), but to achieve a hydraulic conductivity of about 10^{-3} cm/sec the active Bauxsol™ loading can be no more than about 35%. The problem with a low mass loading of active material is that the size of the reactive filter increases substantially to accommodate the inert material. Consequently, there is a need to produce porous media that where hydraulic conductivity can be controlled, and most of the material is actively involved in metal and oxy-anion removal. This paper presents the physical characteristics of a porous material produced that meets these desired engineering criteria.

2 Method

A porous pellet for use with tanning effluents was made in accordance to the specified method (Clark et al., 2004). The pellet consists of a dry powder mix of 65.1% Bauxsol™, or seawater neutralised red mud (Bauxsol™ was used for these investigation, but seawater-neutralised red mud samples provide similar data, i.e. ± 5% of Bauxsol™ samples), 14.9% Ordinary Portland Cement (OPC; the primary cementing agent), 7.9% finely crushed silica sand (fly ash can be substituted) to provide silica to tobermorite gel formation, 3.9% hydrated lime to provide additional Ca and pozzolanic reactions in the system, 7.7% magnesium oxide to provides additional Mg and pozzolanic reactions in the system, and 0.5% HPMC to provide a 3-dimensional network for growth of the tobermorite gel, to provide lubrication in the slurry and to consume excess Na in system. A slurry was then made by adding water and once thoroughly mixed, a solution containing 3% hydrogen peroxide the air entraining agent and 0.32 M H_3PO_4, (to provide phosphate linked stabilisation of air bubbles) was added at a rate of 1% of the dry ingredients. The slurry was then poured in to a mould and bath cured at 4°C for 28 days before being tested for uniaxial compressive strength; five moulds were made for each moisture content.

Pellets were investigated by scanning electron microscopy to determine the extent of gel formation of the fine internal structures, pore space diameters and interconnectedness; interconnectedness was also determined using a 10 mm thin slab in a falling head permeameter. Slake durability testing was carried out in a rotating abrasive drum, over two wet and dry cycles (AS 4133.1.1.51), to determine the percentage loss. Porosity testing was done by placing a 10 cm^3 piece of pellet material in 100 mL of water and subjecting this to a vacuum of 200 mm of Hg, and noting the volume rise in the water.

3   Results

The average uniaxial compressive strengths of the five pellets blocks made with the above recipe and different moisture contents are plotted (Figure 1). These data indicate that maximum strength of the porous pellet is achieve at about 50% moisture, with a rapid decline in strength as moisture content is increased. Although pellets that are made too wet have poor compressive strength they may still be used for water treatment, but cannot be used in tall columns because of pellet compaction and hydraulic conductivity loss. A compressive strength of 5 MPa is the minimum compressive strength of a concrete for use in domestic driveways (BRANZ, 2001). In addition, once the moisture content of the pellet slurry starts to fall below 48%, the slurry mixing and pouring from the mixing bowl becomes difficult. At 42% moisture the mixtures containing fly ash as a substitute for the silica sand, cannot be adequately mixed, and the mixture cannot be poured from the bowl.
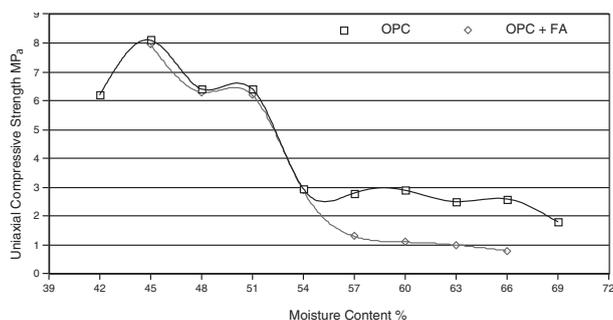

Figure 1. Uniaxial compressive strength of pellets made with varying moisture contents. OPC + FA are pellets where fly ash is used in replacement of the fine silica sand; OPC is Ordinary Portland Cement, and FA is Fly Ash.

SEM investigations of the pellets indicates that there is an open weave lattice-like structure to the pellets and that both macro- and micro-porosity are well formed with a good interconnection between pore spaces (Figures 2 & 3). The vacuum testing of the pellet materials indicates that the porosity ranges from 23% to 35% of the pellet mass; the minimum value obtained from the tests was 20%, which is about 3 times the porosity of a general purpose concrete. The variable nature of the porosity observed in the pellets is also reflected in the broad range of compressive strengths observed for any single moisture content, especially for material produced using a high water content. This variability is a consequence of how quickly the pores created from the escaping gas produced from the breakdown of the hydrogen peroxide, can be fixed in place during the gel formation. At higher water contents the mix is far less viscous than at lower water contents, hence more of the gases produced can escape before gel formation fixes them. In addition, the age of the peroxide, and how it has been stored can also play a substantial role in the degree of pore formation. During preparation of one batch of samples the peroxide needed replenishment, and this change in peroxide gave an increase in porosity from 26% to 34% porosity; hydrogen peroxide had been lost through age.
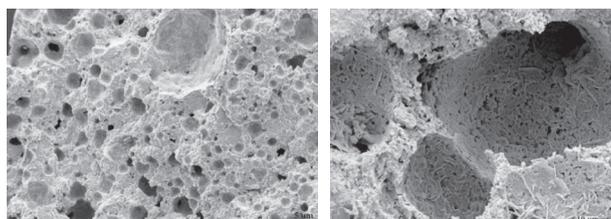

Figure 2 SEM Images of the porous pellets showing the macro-porosity (A), and the fine micro-porosity (B) and open cross hatched mineral binding structures (B). Micro-porosity on the order of 2-5μm penetrates between macro-pores and provides the internal permeability of the formed material.
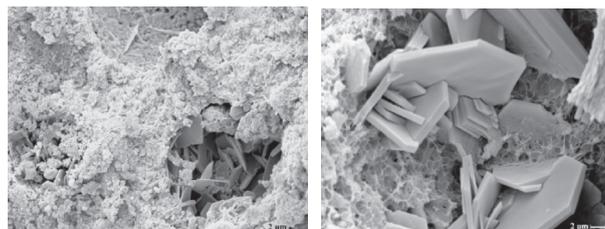

Figure 3. SEM micrograph of a macro-pore containing precipitated Mg- & Ca-hydroxy-carbonates (A), a close view of the precipitates (B); note the open lattice structure of the material binding between the precipitated crystals (lower centre right; B).

In some macro-pores, a mineral precipitate occurs and EDAX analysis indicates that the mineral precipitates are predominantly Mg- and Ca-hydroxy-carbonates (Figure 3). These precipitated hydroxy-carbonates provide a substantial proportion of the additional acid neutralisation capacity of the pelletised Bauxsol™, which is typically raised from 4 to 7 mole/kg. These precipitates are formed from the incomplete consumption of the Mg-oxide and Ca-hydroxide added to the mix as additional pozzolanic material.

The interconnected porosity between the macro-pores gives the pellet an internal permeability of about $5.3–6.1 \times 10^{-6}$cm/sec when tested with tap water, and indicates that pore interconnectedness extends for more than 10mm (thickness of the slab used in the falling head permeameter trials). When these permeability tests were redone using acid rock drainage (ARD) water, the measured permeability increased to 1.2 to 1.5×10^{-5}cm/sec. This sudden increase in internal permeability suggests that some of the precipitated hydroxy-carbonates in the macro-pores have been removed opening new paths between pores, or that some acid attack breaches some of the thin Bauxsol™-cement walls allowing a greater fluid flow between pores. These findings are consistent with findings of Munro et al (2004), who also find that the permeability of Bauxsol™-based treatment barriers is greater when using ARD as a test fluid than tap water, and some of the reasons cited by Munro et al (2004) may also apply here.

Slake durability testing indicates a <6% loss of material for pellets with a water content of 51% during impact-abrasion-rolling; this drops to <4% if the water content is reduced to 48%. These data suggest that the loss of material through physical abrasion and dusting during transport, handling and product emplacement is low. A low slake durability test is desired because a substantial loss of fines may lead to a clogging of permeability in a constructed flow through reaction cell, and may cause Occupational Health & Safety (OH&S) handling constraints during reaction cell emplacement. The slake durability recorded is comparable to that of shales used in embankment construction in Colorado (Anon, 1990).

4   Conclusions

The pelletised material produced here has the physical properties that make it suitable for use in water treatment using flow through reaction cells. Firstly a compressive strengths greater than 5 MPa can be achieved, which means the material will not crush under its own loading, allowing construction of tall columns. Secondly, internal porosity and permeability are sufficient to allow a range of pellet sizes to be graded and to ensure all of the pellet material is available for reaction. Thirdly, slake durability testing indicates a <4% loss of material as fine particles during transport and column construction, or during column operation, which indicates that the engineered hydraulic conductivities can be maintained. Fourthly, the permeability of the treatment column can be controlled by controlling the pellet size, and finally, that the proportion of active treating material is >65% of the treatment column mass.

References

Anon (1990) Standard Method of Test for Determining the Durability of Shales for use as Embankments. Colorado Proceedure CP26–90, Colorado Highway Department 2pp.

BRANZ, 2001. Concrete Driveways, BRANZ Bulletin, Number 412, 8pp.

Clark, M., McConchie, D., Faux, D. and Munro, L., 2004. Methods for the development of porous pellets. Mt Aspiring Geochemical Consultants Pty. Ltd., Australian Patent PCT/AU2004/, pp. 33.

Clark, M., McConchie, D., Walsh, S. and Davies-McConchie, F., 2003. Fertiliser. Nauveau Technology Investments Ltd, Australian Patent, pp. 36.

Hanahan, C., 2001. Treatment of Acid Mine Drainage with Seawater Neutralised Red Mud. PhD Thesis, University of Queensland, Brisbane.

McConchie, D., Clark, M. and Davies-McConchie, F., 2001. Processes and Compositions for Water Treatment. Neauveau Technology Investments, Australian, pp. 28.

McConchie, D., Clark, M., Davies-McConchie, F. and Ryffle, T., 2003. Processes for the treatment of a waste material having a high pH and/or alkalinity. Neauveau Technology Investments, Australian Patent, pp. 34.

McConchie, D., Clark, M.W., Fawkes, R., Hanahan, C. and Davies-McConchie, F., 2000a. The use of seawater-neutralised bauxite refinery residues in the management of acid sulphate soils, sulphidic mine tailings and acid mine drainage, 3rd Queensland Environment Conference, Brisbane, Australia, pp. 201–208.

McConchie, D., Clark, M.W., Hanahan, C. and Baun, R., 2000b. New treatments for the old problems of acid mine drainage and sulphidic mine tailings storage, The 5th International Symposium on Environmental Geochemistry, Cape Town, South Africa, pp. 101.

McConchie, D., Clark, M.W., Hanahan, C. and Fawkes, R., 1999. The use of seawater-neutralised bauxite refinery residues (red mud) in environmental remediation programs. In: I. Goballah, J. Hager and R. Solozabal (Editors), REWAS '99 Proceedings of the Global Symposium on recycling, waste treatment and clean technology, San Sebastian, Spain, pp. 391–400.

McConchie, D.M., 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 (Editors), Proceedings of the 2nd International Symposium on Extraction and Processing for the Treatment and Minimisation of Wastes. The Minerals, Metals and Materials Society, Scottsdale, Arizona, pp. 407–416.

Munro, L., Clark, M. and McConchie, D., 2004. A Bauxsol™-based Permeable Reactive Barrier for the Treatment of Acid Rock Drainage. Mine Water and the Environment, 23: pp. 183–194.