Soil-like conditions can be achieved inorganically in alkaline bauxite residue

Martin Fey[A], Neha Kaur[A] and Ian Phillips[B]

[A]School of Earth and Environment, University of Western Australia, Crawley, WA, Australia Email martin.fey@uwa.edu.au
[B]Alcoa World Alumina Australia, Huntly Mine, Pinjarra, WA, Australia Email Ian.Phillips@alcoa.com.au

Abstract
Achieving a stable cover of vegetation on alkaline bauxite residue is challenging because alkalinity, sodicity, salinity and nutrient deficiency inhibit plant establishment. When the residue sand fraction is used as the growing medium there are additional problems of nutrient loss by leaching and poor water retention. Organic amendments or topsoil are consequently thought widely to be valuable for rehabilitation. Recognising the importance of organic matter for developing soil and achieving a stable ecosystem, we conducted a glasshouse experiment with kikuyu grass (*Pennisetum clandestinum*) to test the feasibility of generating organic matter *in situ* with water, nutrients and sunlight using inorganically amended residue sand. The amendment of the sand consisted of adding 4 % gypsum and 5 % carbonated (CO_2-sparged) red mud together with 150 mg/kg P as phosphoric acid and a range of macro- and micronutrients. Grass was grown by planting discs of turf in 64 pots (90 x 500 mm pipes fitted for leachate collection) each containing 2.9 kg of amended residue which had been leached with about 25mm of water.

Experimental treatments consisted of 16 treatment combinations of 4 leaching frequencies and 4 rates of N application as solutions of ammonium sulfate applied every 4 days and containing maintenance levels of K and Mg. After 3 months, leachate pH had declined from 8.5 to 7.7. Leaching every 4 days for 3 weeks reduced electrical conductivity (EC) of leachate to < 5dS/m and used 1-2 pore volumes (100-200 mm) of water. Maximum dry matter production (roots and shoots) was about 35 g/pot after 3 months. This equates to about 50 Mg/ha. Growth response to N was linear up to the highest N rate of 6470 kg/ha ammonium sulfate. The results suggest that use of a non-invasive, sodium-tolerant grass such as kikuyu, besides providing a protective cover, has considerable potential for generating organic matter and accelerating soil development during restoration of bauxite residue.

Key Words
Bauxite residue, alkalinity, salinity, kikuyu grass, carbon sequestration, gypsum

Introduction
The residue (about 70 million tonnes a^{-1} globally) from digesting bauxite with NaOH for alumina production is caustic and requires considerable amelioration before it will support plant growth. The commonest ameliorant is gypsum which serves as a sink for both soluble and hydrolysable alkalinity through calcite precipitation. This occurs slowly in the presence of atmospheric CO_2 but can be hastened through prior carbonation. At Alcoa of Australia's Western Australia refineries, bauxite-processing residue sand (> 150 µm) is separated and used in constructing outer embankments of residue storage areas, which are subsequently rehabilitated as part of progressive closure. Recent research suggests that mixing a small amount of mud with residue sand might overcome problems of poor retention of water and nutrients which affect vegetation growing on sand, and that excessive alkalinity might be avoided when carbonated mud is used for this purpose.

Methods of field-scale rehabilitation may employ organic amendments such as sewage sludge, compost or woody mulch to improve physical, chemical and microbial properties. It has been suggested that minimising the immobilisation, leaching or volatilization of plant nutrients such as P, N, Mg and some trace elements, by supplying them in slowly biomineralisable form, might be an important advantage of organic ameliorants even though inorganic fertilizers may be cheaper (Eastham *et al.* 2006). The objective of this study was to find out whether, and at what rate, vigorous plant growth could be achieved in residue that has been amended inorganically, the idea being to generate organic matter for soil development without having to import organic amendments or soil materials. Axiomatically, any process that produces organic matter instead of consuming it must achieve a better score for environmental effectiveness, especially if it is cheaper and creates a protective soil cover that subsequently can be managed through succession towards a planned ecosystem.

Methods and materials

The experiment was conducted in a glasshouse using kikuyu grass (*Pennisetum clandestinum*, var. Village Green) in 64 pots filled with residue sand (uncarbonated) from the Kwinana alumina refinery after being amended with the following additions: 5 % carbonated mud (added as a slurry), 4 % gypsum ($CaSO_4.2H_2O$), and 150 mg/kg P (applied as dilute phosphoric acid). Two handfuls of garden soil were added to achieve microbial inoculation prior to final blending. Each pot consisted of a 500 mm length of 90 mm diameter plastic piping fitted with a base perforated with ten 3mm holes, and was filled to 10cm from the top with 2.9 kg of amended residue. The following elements (mg/kg) were then added in a 100ml mixed solution applied to each pot: 50 N as KNO_3 plus 30 N as $(NH_4)_2$ SO_4, 40 Mg as $MgSO_4$, 150 K as KNO_3, 1 B as H_3BO_3, 0.1 Mo as $(NH_4)_6Mo_7O_{24}$, 2 Zn and 1 Cu as sulfates, and 50 Mn as $MnCl_2$. Pots were fitted with a plastic leachate collection bag at the base and mounted on flower pots for stability. A disc of established kikuyu grass, cut by hammering a sharpened piece of the piping through a slab of commercial turf, was placed firmly on the surface of residue in each pot. The pots were lightly watered daily for three weeks in the glasshouse to produce a uniform growth of grass (about 5 cm) which was removed by clipping flush with the top of the pots prior to commencing treatments. These consisted, in 4 replications, of 16 combinations of (a) four leaching frequencies, whereby 200 ml water was either not applied (L0) or applied every 16, 8 or 4 days (L1, L2 and L3,respectively), after watering to field capacity (which was done every 4 days by weighing) and (b) four levels of nitrogen applied every 4 days as 10 ml of solution supplying 0, 3, 6, or 12 mg/kg N as ammonium sulfate (N0, N1, N2 and N3, respectively) and incorporating in the same solution a maintenance application of 16 mg/kg K as KCl and 3 mg/kg Mg as $MgSO_4$. (The molar ratio N:K:Mg in the N3 treatment was thus 0.86:0.41:0.13). Every 4 days prior to irrigation the pots were weighed, and the volume, pH and electrical conductivity (EC) of leachates were measured prior to storage at 4 ^{0}C. Three harvests of grass were cut (1 per month) and the dry mass (60^{0}C) recorded. Columns of residue with roots were extruded from the pots and sectioned into 4 equal parts after slicing away the original turf with stems and stolons. A sub-sample of each section was retained for analysis and the roots were separated by washing on a screen and drying at 60^{0}C.

Results

Before the first application of treatments the pots had been pre-leached and an average of 0.09 ± 0.01 pore volumes of leachate was collected from each pot with an average EC of 78 dS/m and pH of 8.5. A second leaching was applied to the pots after planting and produced the same quantity of leachate with an average EC of 33 dS/m and pH of 8.4. The EC and pH of leachates collected after treatments had commenced are shown in Figure 1.

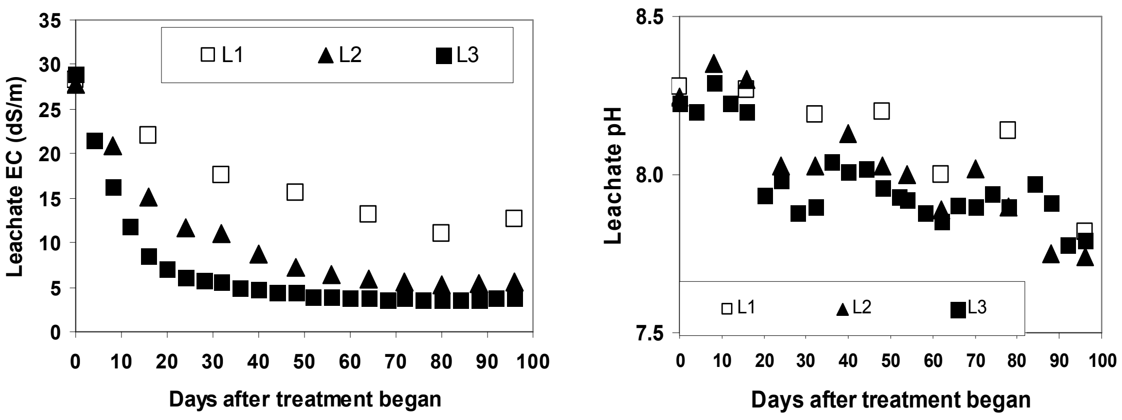

Figure 3. Decline in EC and pH during the course of the experiment after treatments commenced, as a function of leaching frequency (L1: leaching every 16th day; L2: every 8th day; L3: every 4th day).

Leaching frequency affected the rate of decline in leachate EC more clearly than that of leachate pH. The EC decline can be seen (Figure 2) to have conformed approximately to a single pattern when plotted against water applied, and even more so when plotted in relation to volume of leachate collected.

The final cumulative mean yield of shoots (4 replications; 3 clippings) and other plant parts (3 replications) is shown in Figure 3. Positive interaction between leaching and nitrogen level was evident in yields of foliage but not stems, stolons and roots. The first of the 3 clippings showed this interactive tendency more strongly (data not shown), probably because of the larger salinity differences between leaching treatments during the first month.

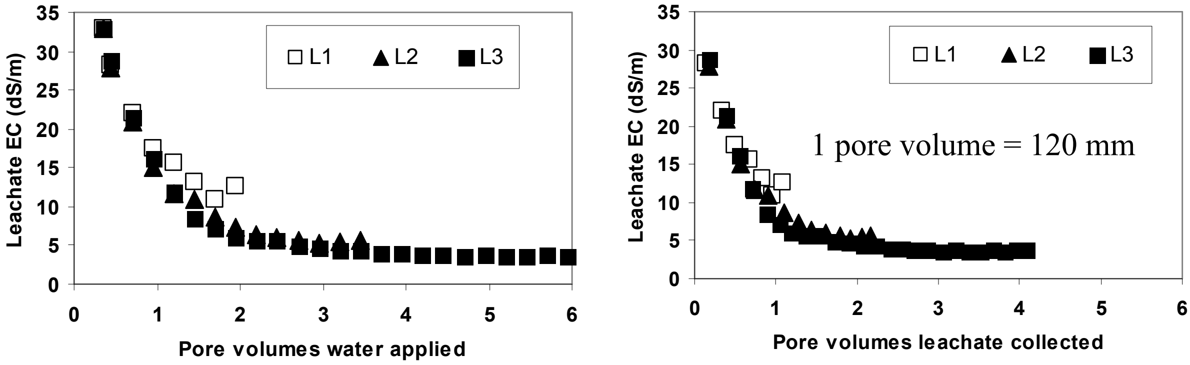

Figure 2. Leachate EC relative to applied water and leachate volume, as a function of leaching treatment.

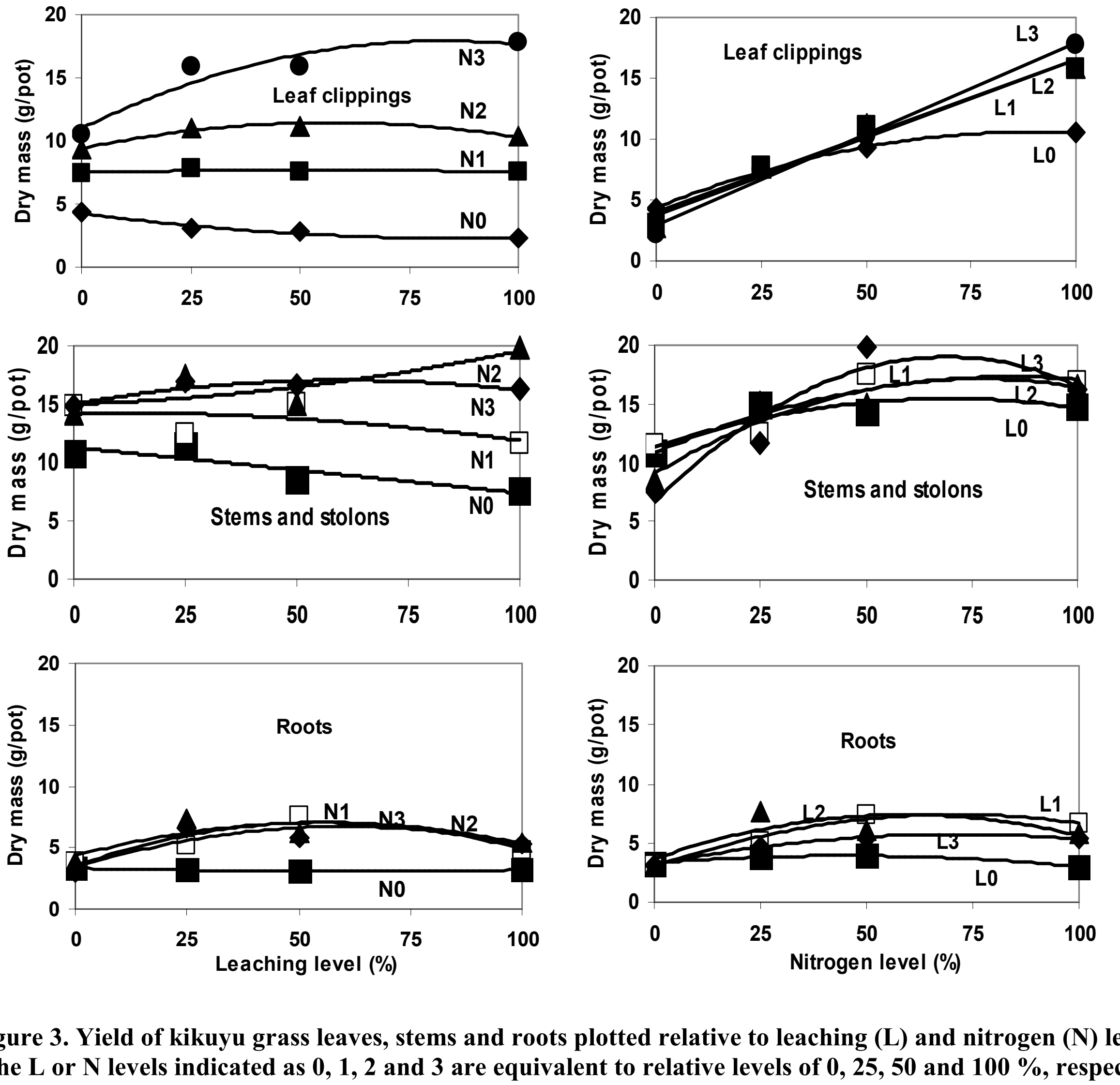

Figure 3. Yield of kikuyu grass leaves, stems and roots plotted relative to leaching (L) and nitrogen (N) levels. (The L or N levels indicated as 0, 1, 2 and 3 are equivalent to relative levels of 0, 25, 50 and 100 %, respectively).

Discussion and conclusions

Analysis of initial leachate from the pots indicated that a tolerable solution pH (~8.5) was achieved with the combined addition of carbonated mud and gypsum but that salinity was severe. X-ray diffraction of salt from dried leachate indicated thenardite (Na_2SO_4). Figure 2 suggests that between 1 and 2 pore volumes of leachate (about 100-200 mm water) removes most of the salt from the 40-cm root zone. This is efficient compared with field observations and is probably due to the uniformity of gypsum reaction. Leaf dry mass in the first month was 1.8 in L0N3 and 4.8 g/pot in the L3N3 treatment, confirming the value of early leaching. The response to N was also large: L3N0 had a corresponding yield of only 1.1 g/pot. After 3 months, N level had induced no effect on pH which varied between 7.6 and 7.9 in leachate and residue. The latter at the top of the pots effervesced with HCl, confirming persistence of carbonate buffering. Further analysis of solids and leachates including total acidity will be needed to quantify nitrification effects. The response to N (Figure 3) was linear up to the highest rate (N3), equal to 1360 kg/ha N or 6470 kg/ha ammonium sulfate. Dry biomass at highest yield levels was about 35g/pot after discounting initial turf mass (~5g). This translates to roughly 50 Mg ha^{-1} in 3 months. About 1/5th of this took the form of roots which extended throughout the volume of all pots. Although direct extrapolation to field conditions is not warranted the results clearly demonstrate substantial C sequestration potential and that alkaline bauxite residue can become a highly productive medium for plant growth with a suitable combination of water and conventional fertilizer salts.

The treatments that collectively produced these results included the following: (a) addition of gypsum, without which sodic and alkaline conditions would remain prohibitive (Woodard *et al.* 2008); gypsum provides Ca for calcite as a sink for alkalinity, thus promoting the dissolution of sodalite; (b) irrigation, to maximize growth response to nutrients and remove excess salts; (c) use of a vigorous strain of sodium-tolerant grass (Mills *et al.* 2004); (d) use of carbonated mud (Khaitan *et al.* 2009) to ameliorate the uncarbonated sand; (e) a generous basal application of macro- and micronutrients; (f) large nitrogen applications as ammonium sulfate in solution every four days, with simultaneous maintenance applications of K and Mg to compensate for leaching losses and possible fixation (e.g. Mg in struvite and K in sodalite or dawsonite); (g) a relatively warm temperature regime (between 15 and 30°C). Many of these treatments were designed to deal with side-effects associated with alkalinity and mineralogy of the bauxite residue. The next step would be to work backwards with subtractive treatments to find out the extent to which each of these factors is limiting. The present results suggest that the expense of organic amendments or imported topsoil (Wehr *et al.* 2006) could be obviated if the residue itself is turned into a suitable growth medium. Intensive propagation of a pasture such as kikuyu (especially a male-sterile strain with limited invasive capacity) could provide a stable cover as a prelude to introducing native plant species for establishing ecosystems similar to Jarrah forest or Banksia woodland. Kikuyu is readily killed with glyphosate. Rapid neutralisation of alkalinity and build-up of organic matter to create soil-like conditions might boost confidence in the rehabilitation process prior closure. Disposal of leached sodium sulfate seems to be the most limiting requirement for success on a field scale and getting it done early makes sense. This applies to whatever revegetation strategy is adopted.

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