

PHOSPHORUS MOVEMENT THROUGH SANDS MODIFIED BY RED MUD

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ABSTRACT

Field and laboratory column experiments show that red mud (waste from bauxite refining) neutralised with gypsum increases Phosphorus (P) sorption capacity of sandy soils. Some 1.68 g P/kg RMG (red mud neutralised by 5% gypsum) was sorbed from 9.5 mg/L P solution during a continuous flow of 50 cm/d for 750 pore volumes. Batch tests indicate almost no desorption of sorbed P, however during continuous flow leaching, a total of 14% of the sorbed P was desorbed. During flooding — drying cycles of laboratory columns, with secondary effluent, 91% P removal occurred through 30% RMG (30% RMG, 70% Bassendean sand mixture), and 63% removal through 20% RMG, both with some more capacity to sorb P; whereas 10% RMG continued to sorb P at 50% efficiency even after the calculated sorption capacity was exhausted. Initially previously sorbed P in soil would be leached out by the alkaline leachate from red mud incorporated above it. In general the potential for P removal by renovated soils seems high.

INTRODUCTION

At Murdoch University, a three year project was conducted to examine the potential of red mud (a waste product from bauxite refining) as a sandy soil modifier for waste management purposes. The project covered characterisation of the properties of red mud neutralised with gypsum, copperas, and other materials,



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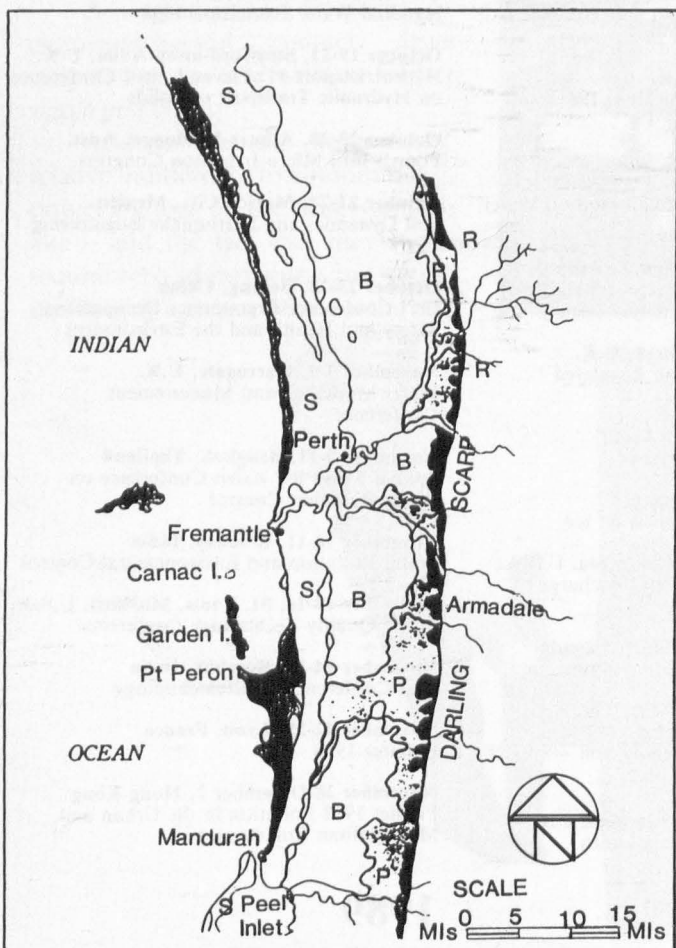


Figure 1. Geomorphic elements of the Swan Coastal Plain. Ridge Hill Shelf (R), Pinjarra Plain (P), Bassendean Dunes (B), Spearwood Dunes (S), Quindalup Dunes (Q). Source: McArthur and Bettenay, 1974.

and investigations by laboratory and field trials of the ability of red mud to renovate waste water through soil infiltration. In this paper, an aspect of this research project, the phosphorus sorption capacity of red mud by laboratory columns is described.

The Swan Coastal Plain, W.A., extends from Geraldton in the north to Dunsborough in the south, and is bounded in the east by the Darling Fault. The Swan Coastal Plain is formed almost entirely of depositional material (McArthur and Bettenay, 1974). The water retention capacity of the Swan Coastal Plain's sands is very low, resulting in limited crop productivity of the soil. A further consequence is the leaching to the receiving waters of nutrients from the fertilizers used to improve soil productivity, a problem reaching major proportions in several large estuaries (Hodgkin, 1984). The sorption capacity of the soil for phosphorus (P) has been found to be very low (Cameron and Ho, 1984), and nutrients in wastewater applied to the sands for groundwater recharge have not been removed before the water reaches the water table (Mathew, Newman and Ho 1982). The application of neutralised red mud has been suggested as a possible solution for P retention (Barrow, 1982; Ho, Mathew and Newman, 1983; Ho, Newman, Mathew and de Potter, 1985; Glenister and Thornber, 1985).

Figure 1 shows the Swan Coastal Plain about the Perth Metropolitan region. Bassendean sand and Spearwood sand occupy most of the area; both are characterised by high saturated

hydraulic conductivity, and low cation exchange capacity (Table 1), particularly Bassendean sand.

The aim of this study was to investigate P movement through the sandy soils of the Swan Coastal Plain modified with neutralised red mud. Consequently the process involved in P movement in these soils was investigated, and an evaluation was undertaken to ascertain whether and to what degree soils modified with neutralised red mud retain P.

TABLE 1. PROPERTIES OF BASSENDEAN AND SPEARWOOD SANDS

Parameter	Bassendean	Spearwood
1. Effective size, mm	0.15 ± 0.01	0.18 ± 0.01
2. Uniformity coefficient	2.4 ± 0.2	1.9 ± 0.1
3. Particle density, g/cm ³	2.61 ± 0.04	2.65 ± 0.01
4. Bulk density, g/cm ³	1.55 ± 0.01	—
5. Hydraulic conductivity, m/day	30 ± 2	16 ± 1
6. pH	4.6	5.6
7. Cation exchange capacity (Ammonium saturation method), meq/100 g	0.56 ± 0.05	1.5 ± 0.2
8. Adsorption equilibrium distribution coefficient for ammonium (mg/kg)/(mg/L)	0.085	0.70 ± 0.04

Source: Mathew *et al.*, 1982.

Characteristics of Red Mud

Red mud from this research was obtained from the Kwinana refinery of Alcoa Australia. The chemical and physical properties of red mud are tabulated in Table 2. Because of its high pH, red mud should be neutralised before mixing with sand. Several neutralising agents were tested for this purpose, the content per 1 kg of dry red mud being gypsum 5%, copperas 7%, 0.59 L of Laporte effluent (acidic effluent from a titanium dioxide manufacturing plant containing waste sulphuric acid and ferrous sulphate), also 0.95 L of 1 M HNO₃, or leaching with 0.01 M CaCl₂ solution, and 0.03 M NaCl solution. Of all these, the most promising (Ho, Newman, Mathew and Parker, 1984). During this study red mud used in the experiments was neutralised with 5% gypsum (CaSO₄·2H₂O waste gypsum from the processing of phosphate rock into superphosphate).

TABLE 2. PROPERTIES OF RED MUD

Hydraulic Conductivity	0.0003 m/d
Total Alkalinity	5.0 g/L as Na ₂ CO ₃
Alkalinity (on dry weight basis)	
In entrained liquor	2.7 g as Na ₂ CO ₃
In desilication product	39.2 g as Na ₂ CO ₃
CEC	20.4 meq/100 g

Source: (Ho *et al.*, 1984).

MATERIALS AND METHODS

Either PVC or perspex columns were employed for the four experiments described below. The soil was packed to a bulk density of 1.5 g/cc. To ensure this, the columns were packed with 1 cm or 2 cm increments of the soil wetted with 5% 0.01 M CaCl₂ solution and compacting it to the desired depth increment. The solution was fed to the columns using the Mariotte Bottle principle or syphon arrangement.

The laboratory experiments were carried out with at least two replicates. Phosphate concentration as phosphorus was determined by the Murphy and Riley Method (1962). Colorimetric determination was performed on a Shimadzu UV-210A double-beam spectrophotometer at a wavelength of 882 nm and slit width of 15 nm using a 4 cm cell. The P solutions were prepared from potassium dihydrogen orthophosphate (KH₂PO₄). The samples were filtered through 0.45 μm pore size membrane filter before being analysed and if not immediately analysed after collection were stored below -10°C.

EXPERIMENTS AND RESULTS

1. Phosphorus Sorption Column Experiment

Batch tests upon several samples of red mud, neutralised by

various agents have indicated that the mud had a high sorption capacity for P (Ho, Newman, Mathew, and Parker, 1984). Accordingly, a column sorption experiment was conducted to test the removal under conditions closer to field conditions.

Two perspex columns, each with 4.3 cm internal diameter, were packed to a 5 cm height with a mixture of 70% Bassendean sand and 30% gypsum neutralised red mud (red mud-gypsum, RMG). The RMG contained 95% red mud and 5% gypsum. The pore volume of the soil after packing was estimated to be 40%. Before the application of P solution the soil columns were backwashed with 0.01 M CaCl₂ solution in order to saturate the soil. A P solution of around 9.5 mg/L concentration was prepared and its pH was adjusted to 7.0. For every 10 litres of P solution 1 mL of chloroform was added to prevent P removal by bacterial action. The columns were fed with the solution using the Mariotte bottle arrangement, and leachate flow was regulated using a peristaltic pump. The superficial velocity of flow was maintained at 50 cm/d. Effluent samples from the columns were collected with a fraction collector, each sample being almost 15 cc in volume, half the pore volume of the packed soil. One of the columns was stopped when the effluent from that column reached about 60% of the initial P concentration, the other column was kept running for a month or so until breakthrough was reached.

Outlet samples were collected daily and pH was measured immediately. The samples were kept at -10°C if P concentration was not immediately determined. Good agreement was obtained between the results of both columns. For up to 20 pore volumes there was no P leaching (Figure 2). Sixty per cent of the initial P concentration was reached at 120 pore volumes. Approximately 99% of initial P concentration was reached after 750 pore volumes had drained through the column, and a total of 54 mg of P was sorbed by that time, corresponding to 1.68 g P/kg RMG.

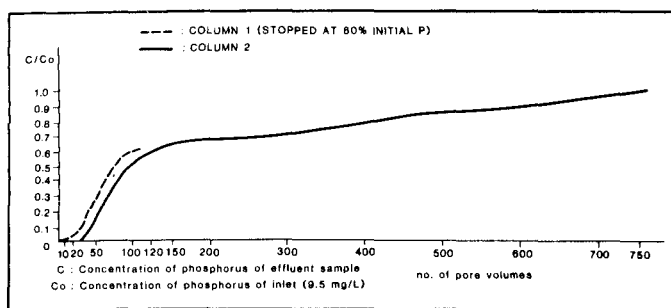


Figure 2. Phosphorus adsorption by red mud-gypsum.

From the batch experiments P sorbed was found to be:

- with 1h contact: 0.86 g/kg
- with 1d contact: 2.6 g/kg

For 5 cm RMG in the columns, the corresponding values should be:

- with 1h contact: 0.0282 g
- with 1d contact: 0.0852 g

With a superficial velocity of 50 cm/d, the residence time of the solution in the 5 cm columns was close to 1 hour. During this period the soil in the column was in contact with solutions of different concentrations, as the sorption capacity of the soil gradually became saturated from the top downwards. Due to continuous flow in the column, gypsum was expected to leach from the soil and hence the retention capacity for P to be reduced. The results indicate that phosphorus sorption by the RMG was much better than the calculated amount from the batch experiment results for a 1h contact time, but less than for a contact time of 1d.

The pH of the samples varied between 7.5 and 8.7 (Figure 3), and did not show any rising trend over the 30 day period. The pattern of the daily measured pH values showed the fresher samples to have a pH about 8.7, higher than samples taken earlier in the day (pH around 7.5). This may have been due to the dissolution of atmospheric CO₂ into the samples before pH was measured.

2. Phosphorus Desorption Experiment

The desorption of the sorbed P in soils has been studied widely (Chakravarti and Talibudeen, 1962; Comargo *et al.*, 1978; Barrow, 1980, 1983; Stuaney and Enfield, 1984).

If neutralised red mud is incorporated into the sandy soils in the field for the purpose of P removal from wastewater or as a

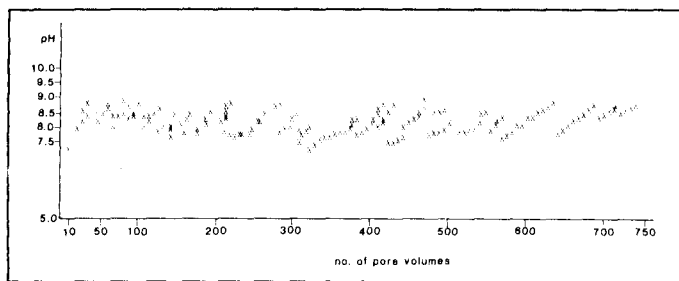


Figure 3. pH values — phosphorus adsorption by red mud-gypsum.

storage for P from fertilizer, the above experiment indicates that P will be sorbed, but it is also expected that some of this sorbed P may eventually be leached by rain. A desorption experiment was carried out to investigate how much of the sorbed P would be desorbed.

The P saturated column of the sorption experiment was leached by distilled water. Initially, three pore volumes of the outlet solution had P concentration equal to the original P concentration (Figure 4). This gradually dropped and at 55 pore volumes became less than 5% of the initial concentration; 7.5 mg of P, (23.4 mg P/kg RMG) was desorbed in total. This amounts to 14% of the sorbed P value, though the results of the batch tests indicated almost none would be leached. During the desorption batch test, RMG was dried following saturation with P, therefore a stronger degree of bonding between P and RMG had taken place. On the other hand, during the desorption column experiment, drying of the soil at 65°C was not carried out. Therefore the desorption of P was easier when the leaching started. The pH of the leachates was between 7.60 and 7.85, which indicate that after leaching of an additional 55 pore volumes, the red mud remained neutral.

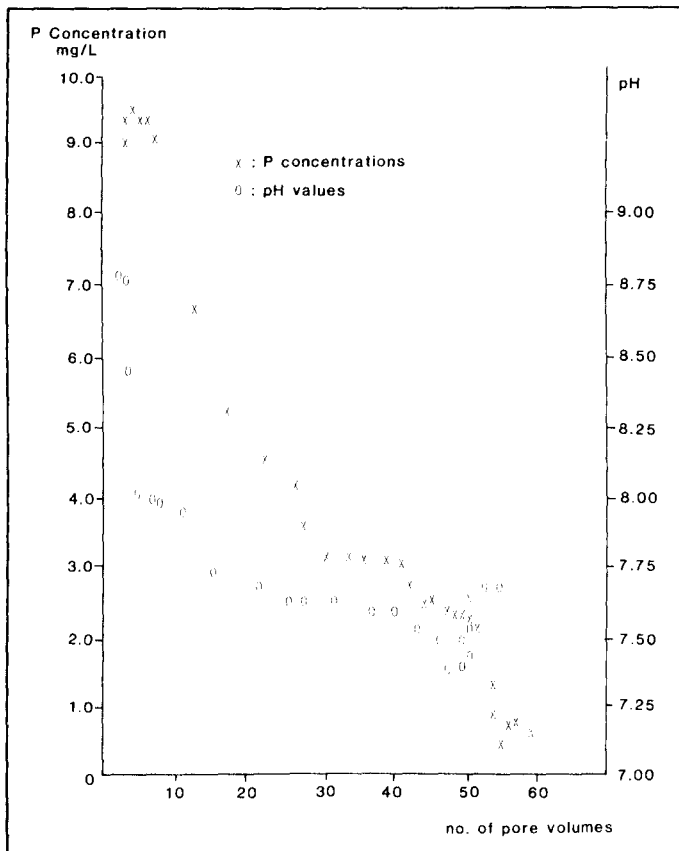


Figure 4. Phosphorus desorption experiment — red mud-gypsum.

3. Column Experiment to Simulate P Removal from Wastewater

The aim of this experiment was to simulate groundwater recharge in Bassendean sand with secondary wastewater in

- laboratory columns. The following aspects were investigated:
 - the optimum percentage of RMG needed to be added to Bassendean sand;
 - the adsorption and leaching of P, NH₄, NO₃;
 - hydraulic conductivity of the columns.

The NH₄ and NO₃ monitoring will be reported separately. In this paper the emphasis is on P sorption.

Three columns were packed with different combinations of RMG and Bassendean sand. In the first column the RMG was 30%; in the second 20%; and in the third 10%. The columns were made of PVC pipes having an internal diameter of 10.45 cm and height of 4.0 m. The lower 0.5 m of the columns were packed with gravel, then 1.5 m with Bassendean sand and above that, 1.0 m of the RMG Bassendean sand mixture. An overhead tank of 26 L capacity was provided for each column. Secondary sewage effluent from the Westfield Wastewater Treatment Plant was pumped to these tanks from a storage tank at ground level. The columns were fed from the overhead tanks through a syphon arrangement.

Cycles of 10 days flooding and 18 days drying were adopted (after Mathew, Newman and Ho, 1982), each cycle taking just under a month. Inlet and outlet samples from the columns were collected every day. After 9 cycles of operation of Column I, and 9 cycles of operation of Columns II and III the following results were obtained: column I removed 3845 mg of phosphorus; at each cycle the removal efficiency was high and the average of 9 cycles was 91%; column II removed 3525 mg of phosphorus and the average removal was 63%; column III removed 4335 mg with a 50% average removal efficiency (Table 3).

TABLE 3. SUMMARY OF PHOSPHORUS BALANCE (Column Experiment Simulating P Removal from Wastewater)

Cycle No.	Influent Quantity mg P	Effluent Quantity mg P	Amount Removed mg P	% Removed
COLUMN I				
1	597	3	594	99
2	629	11	618	98
3	371	9	362	98
4	534	29	505	95
5	527	102	425	81
6	512	118	394	77
7	444	58	386	87
8	352	30	322	91
9	243	4	293	98
Total quantity removed			3845	
COLUMN II				
1	1231	101	1130	92
2	639	365	274	43
3	660	302	358	54
4	880	535	345	39
5	664	283	381	57
6	424	134	290	68
7	492	148	344	70
8	410	7	403	90
Total quantity removed			3525	
COLUMN III				
1	2998	1291	1707	57
2	714	603	111	15
3	937	490	447	48
4	968	620	348	36
5	1123	549	574	52
6	733	275	458	62
7	786	462	324	41
8	512	141	371	72
Total quantity removed			4335	

Removal efficiencies were in accordance with the amount of red mud-gypsum mixture in the columns. With Columns I and II, P sorption capacities were not yet exhausted as compared to batch test results (3845 mg sorption compared to 10036 mg expected capacity for Column I and 3525 mg sorption to 6690 mg expected capacity for Column II). However, Column III sorbed beyond its capacity (4335 mg sorption compared to 3344 mg expected capacity).

A similar situation occurred with the small column sorption experiment (experiment 1 above). In time more phosphorus was sorbed — most probably due to the release of new sites for sorption by way of precipitation during the long experimental period. This is consistent with the findings of Barrow (1982).

4. Experiments with Spearwood Sand

A mixture of red mud-gypsum was applied to the soil at the Kwinana Experimental Recharge Basin. The soil in this area is Spearwood sand. The wastewater applied after the addition of the red mud-gypsum consisted of one third primary and two thirds secondary sewage effluent from the Wastewater Treatment Plant.

Initial samples from the bores and the pans beneath the basin contained similar or higher P concentrations than samples taken before the application of red mud-gypsum — contrary to the expectation that red mud-gypsum would sorb P as the previous batch and column tests indicated.

An experiment was then devised to determine if the occurrence of P in the leachate, after the application of red mud-gypsum at Kwinana Experimental Recharge Basin, was due to alkaline leaching of previously sorbed P from the sand beneath the basin.

Three perspex columns, 4.5 cm internal diameter, were packed, as follows:

Column A contained 20 cm of 30% red mud-gypsum and 70% Bassendean sand.

Column B contained 30 cm of Spearwood sand from the spare recharge basin at Kwinana, which had received secondary sewage effluent for a number of years.

Column C contained 20 cm of red mud-gypsum (30%) and Bassendean sand mixture over 30 cm Spearwood sand.

The columns were leached by distilled water and leachate samples were analysed for P.

Negligible amounts of P (less than 0.1 mg/L) were found in the leachate from Column A as expected from the batch and the large column tests with red mud-gypsum previously discussed.

Column B, which was packed with Spearwood sand alone, contained up to 5.4 mg/L of P which, after 11 litres of water leaching, decreased to a value of 0.4 mg/L. This P would be due to the previous contact of the sand with the sewage. After contact with water containing no P it released these high P concentrations. It can therefore be further concluded that the sand was probably saturated with P at a level around the same as the concentration of P in the effluent (about 10 mg/L).

Column C represented the situation in the field and leached high amounts of phosphorus. The average P concentration was 7.4 mg/L after 1.25 L of leachate had been collected. Since no significant amount of P came from red mud-gypsum (Column A), it must have derived from the Spearwood sand. This amount was higher than the P leaching from the Spearwood sand (Column B). The extra P was probably due to the high pH of the red mud-gypsum leachate (around 8.3-8.5) which shifts the equilibrium towards P desorption from the sand (Figure 4).

This experiment adequately explains the high P concentration in the monitoring bores at the Kwinana Experimental Recharge Basin. It can be expected that the P concentration in the effluent will decline to a very low level in time.

CONCLUSIONS

The results of sorption and leaching experiments indicate that RMG greatly improve the P holding capacity of the Swan Coastal Plain sands. Sorption experiments showed that RMG sorbed P up to 750 pore volumes. During that time a total of 54 mgP or 1.68 gP/kg RMG was sorbed. Moreover, during the application of the first 20 pore volumes no P leached out, with a total of 5.4 mg P/kg RMG sorption. If secondary effluent from a sewage treatment plant (serving 20 000 to 25 000 people, with a daily discharge of 8000 m³) is to be recharged to aquifers through 1 metre depth of RMG modified soil, the area required would be about 17 ha for 1 year continuous flow. During the first 170 days, no P would be expected to leach from the soil beneath the RMG layer. If a leachate of 50% initial concentration is considered acceptable, then with one application of RMG, secondary sewage effluent could be treated for 2.32 years. If on the other hand RMG layer is replaced every year, only 10% of initial P concentration will leach during the second half of the year (after 170 days).

In the case of agricultural application, since the input of P is not continuous and P uptake by plants takes place, replacement of the RMG layer will not be necessary. The results of a simulated rainfall application test showed that only 1% of the applied P (super phosphate as 80 kg P/ha) leached out from RMG in a one-year period (Ho *et al.*, 1984).

During the 8 to 9 months of operation of the column recharge experiment, Column I (30% RMG) was only 38% saturated with P and had a removal capacity of more than 90% and, it continued to be above 90% during a further 11 cycles or 11 months operation. (Ho *et al.*, 1986); Column II was 52% saturated with 63% removal efficiency, and Column III (10% RMG) was over-saturated (1.29 times) in relation to amounts expected from the batch tests, with a removal efficiency of 50%. According to the results of the P sorption experiment mentioned above (experiment 1), during the Kwinana Recharge Basin trials with 1 m of RMG, breakthrough of P should not occur during the first 8 m of infiltration or 16 days of flooding at an infiltration rate of 50 cm/d; furthermore, the RMG in the basin should remove P up to 300 m of infiltration, although the percentage removed would decrease with time. The experiments with Spearwood sand showed that P leaching from the RMG applied layer at the Kwinana experimental recharge basin was from the sand beneath that layer, which had been contaminated with P by a previous effluent discharge to the basin. This leads to the conclusion that RMG application onto sands already containing sorbed P will release P as result of the alkaline leachate from red mud during the initial application of water, however this will soon stop.

Parallel studies at Murdoch showed that RMG modified sand has twice the availability of P to plants, compared to sands alone, i.e. 48 ug/gP compared to 24 ug/gP (Yeates *et al.*, 1984). Another result was the lack of significant difference between the bacterial populations of soils modified with red mud and that of soils in the field without any modification. The only adverse result was the amount of salts added to the groundwater from RMG application which was 20 times that of sand without modification. The amount of salts produced can be reduced by minimising gypsum addition and relying on plants to neutralise it. Other results indicated that concentrations in leachate were only F, 1 mg/L; Cd, 0.02 mg/L; and Fe, 148 mg/L. These are acceptable concentrations for the beneficial uses of the groundwater (Ho *et al.*, 1987).

All these studies lead to the conclusion that red mud in neutralised form such as RMG can be used as a soil modifier for agricultural, as well as secondary sewage effluent recharge purposes. The only technical problem remaining is the ultimate disposal of RMG layers in the field when their sorption capacities are exhausted and/or their alkalinity is leached out. However, bringing together two wastes, namely gypsum and red mud appears to result in an environmentally acceptable and useful product.

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Continued on page 45