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*"Water-Every Drop is Precious"*

# PHOSPHORUS REMOVAL USING BAUXITE REFINING RESIDUE (RED MUD)

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## SUMMARY

The removal of phosphate-phosphorus from drain water using bauxite refining residue was investigated by conducting tests mixing phosphate solution with red mud, and red mud neutralized with phosphogypsum or copperas. Phosphate adsorption isotherms (24 h) followed Freundlich relationship with red mud amended with acidic calcium sulphate and ferrous sulphate having up to 18 times adsorption capacity compared to untreated red mud. Experiments contacting phosphate solution with red muds for 30 seconds followed by 24 h settling to simulate proposed removal of phosphate from drain water flowing to the Peel Harvey estuary in Western Australia indicate that up to 97% phosphate removal is achievable.

## INTRODUCTION

Phosphorus applied as fertilizers to agricultural land is a major contributor to phosphorus enrichment of surface waters leading to eutrophication of these water bodies and the associated problems of algal blooms, depletion of oxygen from the decay of the algal biomass, odour, proliferation of insects and elimination of many aquatic organisms. In the sandy soils of the Swan Coastal Plain in the south west of Western Australia superphosphate application in agriculture and intensive animal production has resulted in a severe eutrophication of the Peel Harvey estuary, located approximately 80 km south of Perth, Western Australia (Figure 1). The sandy soils result in applied phosphorus being leached to the unconfined aquifer and then to drains leading to the estuary. Many of the drains were deepening of natural drainage of low lying lands to enable the surrounding areas to be used for agriculture. To maintain high agricultural productivity more fertilizers have been applied to compensate for leaching losses of up to one third of the applied amount (Schofield *et al.*, 1985).

A major drainage system contributing phosphorus to the Peel Harvey estuary is the Harvey river. It contributes 52% of total phosphorus to the estuary, which is carried to the estuary during the winter rain season. The phosphorus is mostly in the form of soluble phosphate rather than particulates, having been leached through soils.

Management options to overcome the eutrophication of the Peel Harvey estuary include weed harvesting, modified fertilizer application and the use of slow-release fertilizers, creation of a new channel to connect the Harvey estuary and the ocean, amendment of sandy soils with bauxite refining residue (red mud), and changes in land use from agriculture to forestry or parkland (Department of Conservation and Environment, 1984).

Weed harvesting is a short term measure, cosmetic in nature and has to be done continually at an annual cost of approximately \$150,000 (Peel Harvey Study Group, 1985). Application of slow release fertilizers can potentially reduce phosphorus leaching by 30% and will save farmers \$40,000 per annum; a community education programme is required to change farmers' practices and will take time. A 2km 200 m channel connecting Harvey estuary and the ocean will increase phosphorus loss to the ocean by up to 50% at a cost of \$31 million and an annual maintenance cost of about \$500,000. Amendment of sandy soils with bauxite refining residue will reduce phosphorus leaching to negligible level in the long term at a cost of \$22 million (Hodgkin *et al.*, 1985). Changes in land use will require community consultation and will take time. All options have their advantages and drawbacks, and two or three options are needed in the long term to limit algal blooms to not more than once in every five years on average. Obviously all options will incur cost to the community.

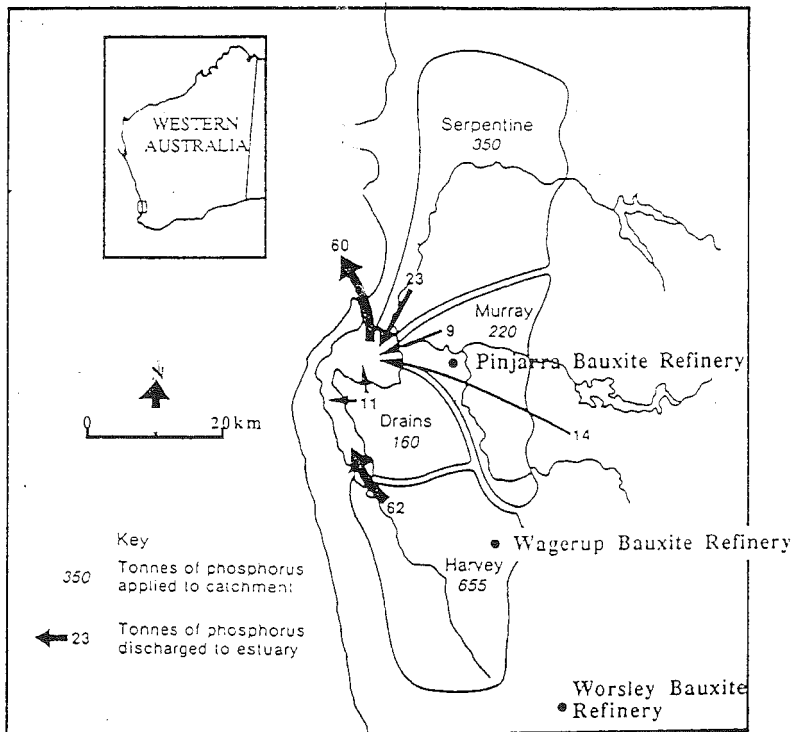


Figure. 1 Peel Harvey estuary and sources of phosphorus

Currently weed harvesting is implemented, as is a programme to induce farmers to change fertilizers management practices (e.g. provision of soil testing and advice). Option beyond these is either construction of a new channel or amendment of sandy soils with bauxite refining residue. Amendment of sandy soils with bauxite refining residue overcomes the problem at the source and is cheaper than the channel option, but will need to involve many farmers and take longer to implement.

Conceptually the soil amendment option is attractive since three major alumina refineries are located close to the catchment of the Harvey river (Figure 1). Western Australia produces about 20% of the world's annual alumina (5.5 million tonnes), and 11 million tonnes of bauxite refining residue. Laboratory and field trials have shown that the amendment significantly increases fertilizers retention, water holding capacity and hence pasture yields of up to 700% (Ward, 1983, 1986; Ho *et al.*, 1989; Vlahos *et al.*, 1989).

An extension of the idea of amendment with bauxite refining residue is to initially mix Harvey river water with the bauxite refining residue to achieve a two

fold result (Humphries & Croft, 1983). While the soil amendment programme is being carried out, phosphorus in the river water will be removed by the residue, and simultaneously the residue will be washed of residual salts. It can also therefore be applied to catchments of fresh water bodies if desired.

The annual flow rate of drainage water in Harvey drain is approximately 300 million kilolitres with a phosphate-P content varying from 1 to 5 mg/L. Red mud production from a nearby alumina refinery is about 700,000 tonnes per year. To treat the entire quantity of flow with the available red mud the minimum ratio possible of water to red mud is about 400.

The concept behind the proposal is that red mud is initially stored in a storage/mixing basin. During the rainy season the drain water is mixed with red mud in the basin and pumped to a sedimentation basin. Estimated mixing time between the red mud and drain water is 30 seconds (in pipeline mixing) and settling time in the sedimentation basin is 24 hours. Overflow from the sedimentation basin is then allowed to drain to the estuary.

The objective of this paper is to present results of laboratory tests to determine whether phosphate removal by red mud could be achieved with the high water to red mud ratio with a short contact time, and whether the quality of the water would be suitable for discharge to the estuary.

## MATERIALS AND METHODS

Red mud received from Alcoa of Australia had 35 % moisture containing 5.0 g/L alkalinity as  $\text{Na}_2\text{CO}_3$ . Additional alkalinity in red mud is in the desilication product and was approximately equivalent to 3 g  $\text{Na}_2\text{O}/100$  g of dry red mud in the mud supplied. The major minerals in the red mud are silica, haematite, aluminous goethite, boehmite and gibbsite.

Practical neutralizing agents for red mud are available in the form of wastes from industries not far from the alumina refineries. Phosphogypsum (also simply referred to as gypsum in this paper) is a waste product from the manufacture of superphosphate from phosphate-rock. The gypsum contained soluble fluoride (0.4 %) originally in the phosphate-rock and residual acid after economic washing (pH 2.7). Properties of red mud and phosphogypsum have been detailed by Glenister and Thornber (1985). Copperas and Laporte effluent were byproduct and wastes from the manufacture of titanium dioxide from ilmenite ore. The titanium production process has now been converted from the sulphate to a chloride process, and the effluent is no longer produced, but copperas is also a waste product of metal cleaning operation using sulphuric acid. Laporte effluent used contained 101.1 g/L  $\text{H}_2\text{SO}_4$  and 87.8 g  $\text{FeSO}_4$  (Ho *et al.*, 1984). The copperas contained 91.5 %  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and a moisture content of 7.8 % (Ho *et al.*, 1985).

Adsorption isotherm of phosphate by red mud and neutralized red mud was determined to study the influence of neutralization on phosphate adsorption. Subsequently batch tests were carried out to investigate desorption of phosphate from red mud and red mud gypsum, followed by tests where phosphate solution was briefly contacted with red mud or neutralized red mud followed by settling of the mixture to determine the extent of phosphate removal and the quality of supernatant after settling.

Samples for adsorption isotherm experiment were prepared as follows.

Red mud (untreated): Red mud was air dried and gently crushed to pass through a 1 mm sieve.

Red mud (leached): A slurry was made by thoroughly mixing 500 g of red mud and 1 L of 0.03 M NaCl

solution. Particles were allowed to settle overnight and the clear supernatant was syphoned off. This was repeated three times to ensure that all dissolved salts were removed except the 0.03 M NaCl. The mixture was allowed to drain in a Buchner funnel fitted with a filter paper and washed with 200 mL of isopropyl alcohol in 50 mL batches. The red mud was dried and gently crushed to pass through a 1 mm sieve.

Red mud gypsum: To 200 g of dried and crushed red mud was added 5 % by weight of phosphogypsum and 200 mL of water. The mixture was kept stirred overnight using a magnetic stirrer. It was then filtered in a Buchner funnel and washed with 1 L of water in 200 mL batches. The red mud was then dried and crushed to pass a 1 mm sieve.

Red mud Laporte effluent: To 200 g of red mud was added 118 mL of Laporte effluent. The mixture was kept stirred overnight and subsequently treated as for the preparation of red mud gypsum.

Red mud nitric acid: Instead of Laporte effluent, 190 ml of 1 M  $\text{HNO}_3$  was used. Preparation procedure was the same as for red mud Laporte effluent.

### Adsorption isotherm of phosphate by red mud

To 20 g of red mud in a 250 mL Erlenmeyer flask, 50 mL of phosphate (prepared from  $\text{KH}_2\text{PO}_4$ ) solution in 0.03 M NaCl background electrolyte was shaken for 24 hours in a shaking water bath at 25 °C. The mixture was centrifuged and the phosphorus concentration of the supernatant liquid determined colorimetrically (Murphy and Riley, 1962). The pH of all samples was measured before centrifuging.

### Desorption of phosphate from red mud and red mud gypsum

Since red mud and phosphogypsum contained phosphorus an experiment was carried out to determine desorption of phosphate-P when red mud or red mud gypsum was contacted with water.

To 20 g of red mud or red mud gypsum was added 50 mL of water. The mixture was shaken vigorously for half an hour to ensure a uniform slurry, then kept in a shaking water bath at 25°C for 24 hours. The phosphate-P concentration of the solution was measured after centrifuging and filtering the sample. Duplicate samples were used. The above procedure was repeated with a red mud water ratio of 1:10 (5 g red mud and 50 mL water).

### Removal of phosphorus from drain water using red mud

Slurried red mud (total alkalinity adjusted to 10 g/

L and moisture content to 50 % to reflect red mud pumped from the refinery to a storage/mixing basin) was vigorously mixed with water containing phosphate (background electrolyte 0.03 M NaCl, pH = 7) in a measuring cylinder for 30 seconds and the mixture was allowed to settle for 24 hours. pH, turbidity, phosphate-P, Na, Ca, Cd and F content of the supernatant liquid were then measured. The latter two parameters were measured to see if significant levels would result from the use of phosphogypsum.

Parameters varied were:

Water red mud ratio: 200 to 1,600 mL/g (equivalent to m<sup>3</sup> water/tonne red mud), straddling estimated ratio of 400

Phosphate-P in water: 1 to 5 mg/L

Red mud amendment: red mud (untreated) red

mud gypsum (prepared as for adsorption experiment, but without washing) red mud copperas (7 % copperas was used instead of 5 % gypsum)

## RESULTS AND DISCUSSION

### Adsorption isotherms

The isotherms follow fairly straight lines on the log-log plot (Figure 2) and indicate that they are well described by Freundlich relationship

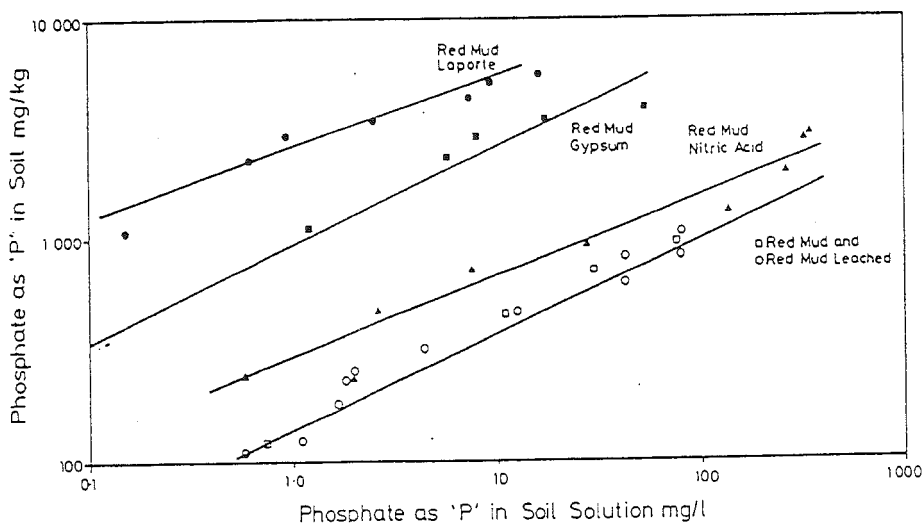
$$S = m C^n$$

where S = concentration of P in red mud (mg/kg) C = concentration of P in solution (mg/L) m, n = constants

Values of m and n are shown in Table 1.

**Table 1.**  
*Freundlich constants for phosphorus adsorption by red mud*

	m	n	pH
Red mud (untreated)	140	0.42	11.0
Red mud (leached)	140	0.42	10.3
Red mud nitric acid	290	0.36	8.0
Red mud gypsum	900	0.44	8.3
Red mud Laporte effluent	2,600	0.33	7.1



**Figure 2.** Phosphate adsorption isotherms

Untreated red mud and red mud leached with sodium chloride had nearly the same adsorption capacity. The pH values were high and fairly close. Red mud neutralized with nitric acid showed double the adsorption capacity of untreated red mud. It is evident that as alkalinity and  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  ions were leached and pH lowered red mud could adsorb more phosphate.

Red mud gypsum showed an even higher adsorption capacity. The presence of calcium might have contributed to the removal of phosphate by precipitation. Red mud neutralized with Laporte effluent showed the highest removal capacity. Precipitation of iron from Laporte effluent could be

the major reason for the higher capacity, since freshly precipitated iron oxides can adsorb a large amount of phosphate.

#### Desorption of phosphorus from red mud

Phosphorus was leached from both red mud and red mud gypsum which had no phosphate applied (Table 2)

The amount leached was significantly higher when gypsum was not added, indicating that gypsum reduced pH and enhanced phosphate retention. Water saturated with phosphogypsum contained about 30 mg/L phosphate (Glenister & Thornber, 1985).

**Table 2.**  
*Phosphate-P desorbed from red mud*

	Red mud water ratio	Phosphate P in solution, mg/L	Phosphate-P desorbed, mg/kg
Red mud	2.5	1.44	3.61
Red mud	10.0	1.03	10.30
Red mud gypsum	2.5	0.026	0.07
Red mud gypsum	10.0	0.014	0.14

#### Removal of phosphorus from drain water using red mud

Phosphorus removal increased with a decrease in the water red mud ratio. The maximum removal with unamended red mud was only 34 %. Gypsum amended red mud removed a maximum of 47 %, while the removal with copperas amended red mud reached 97 %. These results are consistent with the results of the adsorption isotherm experiment, and point to the desirability of using red mud neutralized with copperas.

The amount of phosphate removed by untreated red mud is fairly close to that calculated from the adsorption isotherm, but the amount adsorbed by

red mud gypsum is only similar to that of untreated red mud (Figure 3). It is likely that the high water red mud ratio dissolved the added gypsum (solubility 2.1 g/L). The amount of phosphate adsorbed by red mud copperas is lower than calculated from the adsorption isotherm of red mud Laporte effluent. It is about the same as calculated from the adsorption isotherm of red mud gypsum.

In terms of supernatant quality treatment of the water with copperas amended red mud produced the most satisfactory pH (7.6 - 8.5). With gypsum amended red mud the pH was still satisfactory (7.9 - 8.5), while without any amendment of the red mud the resulting pH was rather high ( 8.2 -10.3).

Generally the turbidity of the water after settling of the red mud was satisfactory (15 - 28 NTU) with an average of about 20 NTU. The appearance of the water was clear.

In general the quality of the water after treatment with red mud had not changed significantly. This is to be expected with the degree of dilution of the

already low concentrations of possible contaminants in the red mud and amendments. The increase in Na concentration was generally less than the experimental error in Na determination. Calcium concentration increase was less than 60 mg/L. Fluoride concentration was less than 0.7 mg/L in all samples while Cd was less than 0.07 mg/L (detection limit of our atomic absorption spectrometer).

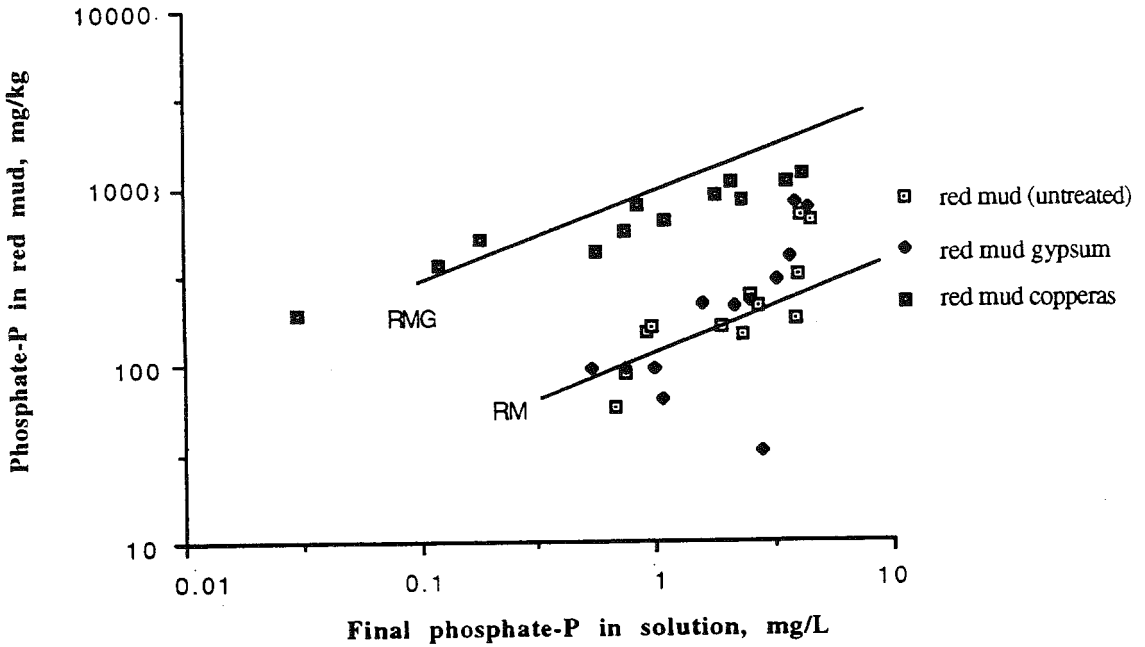


Figure 3. Phosphate adsorbed by red mud in rapid mixing (30 s) followed by settling (24 h) Solid lines are adsorption isotherms (RM = red mud; RMG = red mud gypsum)

The above results show that red mud neutralized with copperas can strip phosphate from drain water with a high degree of removal when employing a rapid mixing followed by settling. Technically the operation will involve the use of red mud slurry pumping, in-pipe mixing and settling in basins. The technology is already practiced in bauxite refineries. The capital cost of this scheme if implemented for the Harvey river and using red mud from the Wagerup refinery is estimated at \$16 million, with an annual operating cost of \$ 2.5 million. In the context of options beyond weed harvesting and modified fertilizer management practices this option is in the same cost category as building a new channel and amending sandy soils with red mud.

There is however scope for application of the technique to smaller drainage systems by incorporation of red mud copperas into a wetland, either natural or man made, intercepting a drain. Specially selected wetland plants can take up phosphorus adsorbed onto the red mud thus maintaining the adsorption capacity of the wetland in the long term accompanied by plant harvesting.

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