

# A Review of Acidic Groundwater Remediation in the Shoalhaven Floodplain in Australia

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**ABSTRACT:** Acid sulfate soils can be found around low-lying coastal floodplains. Acidic groundwater generated from acid sulfate soils creates adverse conditions to vegetation and aquatic life and corrodes steel and concrete infrastructure. As long as these soils are undisturbed and below the groundwater table, they are chemically inert. Therefore, it is important to maintain the groundwater table above the sulfidic soil horizon. Modified floodgates and weirs have been implemented in these low-lying areas to improve water quality. Nevertheless, these methods are not promising in low-lying areas because of the risk of flooding. As a solution, a pilot-scale permeable reactive barrier was installed and has proven to be a promising technology for long-term remediation. This paper presents a review of the above mentioned methods used for acidic groundwater remediation in coastal Australia with detailed field verification data.

**KEYWORDS:** Acid sulfate soils, Acidic groundwater remediation, Permeable reactive barrier

## 1. INTRODUCTION

Pyrite is the main source of sulfidic minerals in acid sulfate soils (ASSs). When the groundwater table falls below the pyritic soil horizon (e.g. during the drought period), sulfidic minerals become oxidised and generate sulfuric acid. Moreover, high concentrations of dissolved iron (Fe) and aluminium are (Al) leached out to groundwater (Dent, 1986). Acidic groundwater rich in dissolved Fe and Al create unfavourable living conditions. Massive fish and oyster kills have been reported and the damage has been estimated as several million dollars in New South Wales and Queensland states (Indraratna et al., 1995). Aquatic marine organisms (e.g. fish, shellfish, worms and oysters) in Australia experience death and red-spot disease (EUS, epizootic ulcerative syndrome) as a direct effect of acidic groundwater. Furthermore, vegetation has undergone severe damage due to the high acidity in soil, directly affecting the dairy farming industry in Australia. One of the main impacts is the influence of acid scalds on plant growth. ASS scalds are bare lands where pyritic soil layers are close to the subsurface because of lack of alluvium soil or where the overlying peat layer has been washed away or burned. High concentrations of Al create a toxic environment resulting in poor growth of plants. Major nutrients and trace elements cannot exist in soils below pH 4, and the soluble heavy metals present in soil under acidic conditions are injurious to plant growth (Rorison, 1973). These high concentrations of Al and Fe restrict plant growth and promote grass, which can tolerate the acidity such as smartweed (Sammut et al., 1996).

ASS also has adverse effects for infrastructures due to acidic groundwater generated in ASS terrain. White and orange-red precipitates formed from Al and Fe, respectively, clog pipes and sewers. A common problem seen in coastal Australia is acid attack on concrete and steel infrastructures like building foundations, bridge piers and pipelines, which weakens the concrete, and rusts the steel reinforcing. ASS has high volumetric moisture content and a low bearing capacity, because of which foundations built in ASS areas require extensive reinforcements to compensate for subsidence and failure (Dent, 1986).

Research on ASS, and remediation methods emerged in the 1980s in Australia. Various remediation methods such as floodgates and weirs have been practiced and are currently being used by government and private sectors to minimize acidification and

decrease the oxidation of ASS. As long as ASS can be left undisturbed, that would be the best method to minimize the impacts from ASS, which is cost effective and eco-friendly.

The ASS research team from the University of Wollongong (UOW) have implemented four engineering solutions to overcome this problem in the Shoalhaven Floodplain in coastal Australia. Figure 1 shows the distribution of ASSs in the Shoalhaven Floodplain and the location of the engineering solutions adopted.

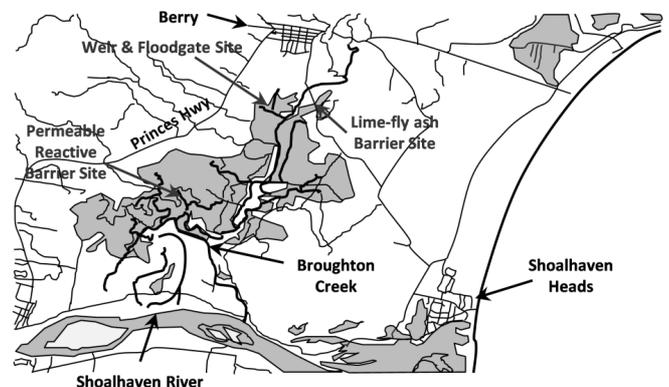


Figure 1 Distribution of acid sulfate soil in the Shoalhaven Floodplain

One of the engineering solutions implemented were v-notch weirs, which has the ability to maintain the groundwater table above the sulfidic soil horizon, thus preventing further acid generation. Another strategy is modified two-way floodgates, which allow tidal water to flow into drains, thereby buffering the acidity before entering the main waterways. Semi-impermeable horizontal lime-fly ash barriers have also been used for their ability to neutralise the acidity and reduce oxygen movement downwards through the soil profile. The latest remediation method adopted is a permeable reactive barrier (PRB), which neutralises the acidic water while groundwater moves through the barrier. This paper showcases the performance of each method and provides a detailed summary of their advantages and disadvantages.

## 2. ENGINEERING SOLUTIONS

### 2.1 V-notch weirs

As discussed previously, maintaining the groundwater table above the ASS horizon can prevent the exposure of ASS to atmospheric O<sub>2</sub>, thus preventing oxidation. Groundwater manipulation techniques have been practiced before in acid rock drainage and have been successful for diminishing the oxidation of tailings by total inundation of acid producing supplies (Pedersen, 1983). UOW researchers (Indraratna et al., 1995, Blunden et al., 1997) have found that the handling of water levels of flood mitigation drains can also affect the surrounding groundwater in ASS. The simple v-notch weirs installed by the UOW research team (Indraratna et al., 1995) (Figure 2) could decrease acid production by keeping the water table over the pyritic soil horizon in ASS terrain of coastal Australia.



Figure 2 V-notch weir (after Banasiak (2004))

A finite element model developed by Blunden et al. (1997) revealed that the installation of weirs would permit the groundwater table to rise to a certain level without flooding. Therefore, preliminary modelling work was carried out by Blunden and Indraratna (2000), in which they undertook a detailed field and numerical study to uphold an elevated groundwater level above the pyritic soil horizon by installing three v-notch weirs near Berry, south east NSW. As a successful outcome of the research carried out at UOW, water manipulation through weirs has been used in coastal Australia over the last decade. This is a cost effective management strategy, which can avoid further pyrite oxidation.

Figure 3 compares the groundwater table fluctuations before and after the installation of the weirs. After the installation of the weirs, the groundwater table was mostly above the pyritic layer. Although the pyrite oxidation was minimised and acid discharge was reduced, the weirs could not improve the long-term groundwater quality. According to Banasiak (2004), the pH was around 4, and dissolved Fe and Al remained high after the installation of the weirs. This implied that the weirs can prevent acidic groundwater generation, but cannot treat the stored acidity.

### 2.2 Self-regulating tilting weir

With the same basic mechanism of v-notch weirs with slight upgrading of the design, self-regulating tilting weirs were installed adjacent to the flood mitigation drains in ASS terrain. According to Blunden (2000) groundwater table heights measured at the field site at Berry, and the results obtained from modelling, showed that noteworthy improvements can be made to minimize the volume of pyritic soil exposed to air.

Similar to v-notch weirs, the self-tilting regulating weirs also maintained the groundwater table above the sulfidic soil horizon, but were not able to improve the groundwater quality. The groundwater pH remained low (Figure 4) and high concentrations of dissolved Al and Fe were observed.

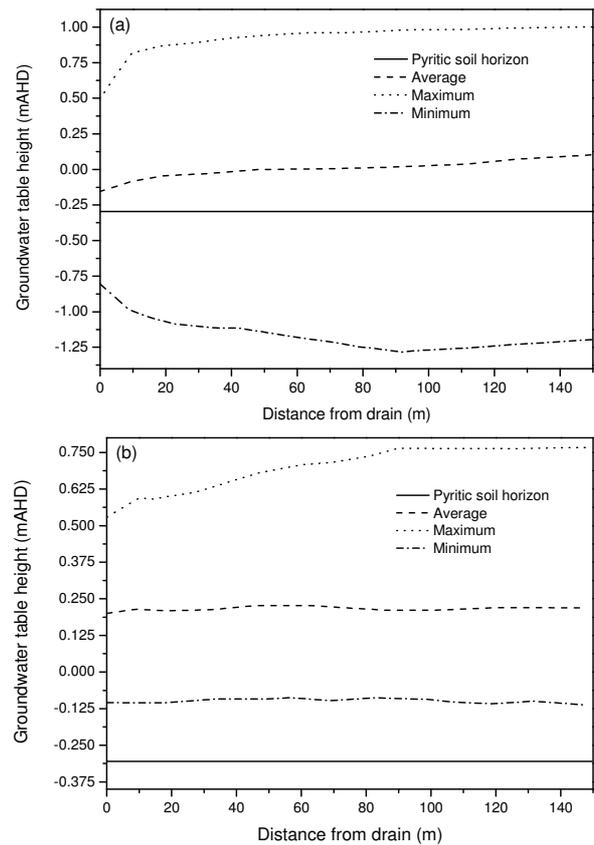


Figure 3 Groundwater table heights (a) before and (b) after weir installation, with maximum and minimum elevations (modified after Golab and Indraratna (2009))

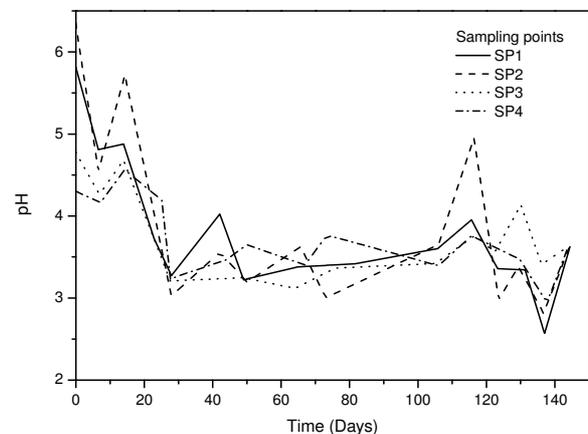


Figure 4 pH profiles at different sampling points (SP) 1-4 (modified after Earnshaw (2001))

### 2.3 Modified floodgates

Two innovative floodgates were developed by UOW researchers (Glamore and Indraratna, 2004, Glamore and Indraratna, 2002, Indraratna et al., 2002) as a substitute to weirs and one-way floodgates near the town of Berry, south east NSW. The first type of modified floodgate provided manual vertical alteration of the floodgate flap and allowed full tidal intrusion within the drain while controlling the flow conditions. Secondly, sophisticated technology was adopted, which was capable of automatically adjusting the gate to control tidal ingress within the drain. Modified floodgates were used to allow tidal flushing into the flood mitigation drain. According to Glamore and Indraratna (2001) and Indraratna et al.

(2002), modified floodgates were designed to decrease the acid reservoir effect, decrease the hydraulic gradient between the drain and groundwater, increase dissolved oxygen, and diminish Al flocculation.



Figure 5 Modified two-way floodgate (Photo courtesy: Glamore (2003))

The water quality of the flood mitigation drain was enhanced after the installation of the modified floodgate (Figure 5). The results obtained from the two-way floodgate show that the drain water quality was improved substantially upon re-establishment of tidal flushing. Moreover, surface water quality continuously measured for three years also showed a raise in drain water above pH 6 (Figure 6), confirming its suitability for ASS remediation. Furthermore, Al and Fe were removed by precipitation as their oxy/hydroxides during tidal buffering (Glamore, 2003).

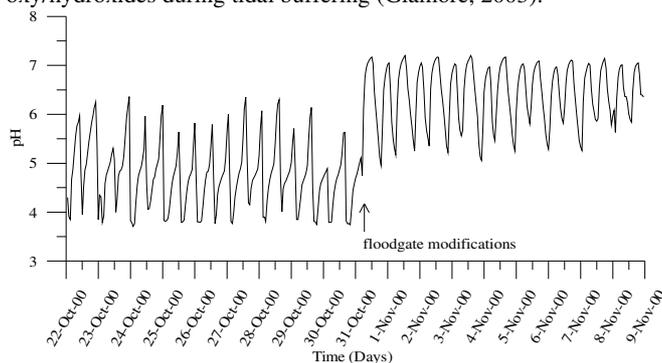


Figure 6 pH before and after the installation of modified floodgate (after Banasiak (2004))

Glamore (2003) reported that the performance of these floodgates was not sufficient especially in heavy rainfall events as the amount of alkalinity generated was not enough to buffer the acidity within the flood mitigation drain. This is because the efficiency of tidal buffering relies on several factors such as the concentration of buffering materials, acidity within the drain and the hydrodynamics of the creek such as flow velocity (Indraratna et al., 2005). Two-way floodgates have a risk of elevating the water table

in low-lying areas and are, thus, not suitable during heavy rainfall events. This sophisticated technology demands frequent maintenance to function properly including the cleaning of sensors and ensuring that debris has not clogged the system.

#### 2.4 Lime-Fly ash barrier

Banasiak (2004) installed a horizontal semi-impermeable lime-fly ash barrier (Figure 7) in the Shoalhaven Floodplain near the town of Berry. An alkaline slurry was injected at low depth above the pyrite layer by radial grouting. The alkaline slurry consisted of fine grained lime, water and fly ash with the proportions of 2:2:1 and was injected according to a grid pattern.



Figure 7 Lime-fly ash barrier at 1m below ground surface (after Banasiak (2004))

According to Banasiak (2004), acidic pH increased to values between 4.5 and 5.5, and the electrical conductivity of the groundwater was comparatively stable after the installation of the barrier, which indicated a decrease in pyrite oxidation. The average concentrations of acidic cations  $Al^{3+}$  and  $Fe^{2+}$ , and other cations  $Ca^{2+}$  and  $Mg^{2+}$  and anions  $Cl^-$  and  $SO_4^{2-}$  decreased in the groundwater at the study site after the installation of the barrier. The lime-fly ash barrier showed better success in raising the groundwater pH and reducing the concentration of pyrite oxidation products (dissolved Al and Fe) in the groundwater than that of the self-regulating tilting weir. Although there was an improvement in groundwater quality, it was not sufficient to adopt this method as a long-term remediation technique.

#### 2.5 Permeable reactive barrier

A pilot-scale PRB (17.7 m long x 1.2 m wide x 3 m deep) was installed in October 2006 (Figure 8 (a)). The cut and fill method was used after detailed geotechnical investigations were undertaken at the field site, and the barrier was installed parallel and 15 m away from the flood mitigation drain. The PRB was placed at the maximum groundwater intersection point, so as to minimize bypassing of the barrier. A geotextile was laid over the trench and was filled with crushed recycled concrete particles of  $d_{50} = 40$  mm. The purpose of using the geotextile material was to protect the reactive media from physical clogging by clay particles and other fine debris flowing through the barrier with the groundwater. Piezometers, observation wells and data loggers were placed up-gradient, within the PRB and down-gradient in order to monitor water quality parameters in an efficient and timely manner. Currently there are 36 observation wells, 15 piezometers and three data-loggers onsite (Figure 8 (b)). Measuring log pH, dissolved oxygen, temperature, salinity etc.

The concentrations of the dominant ions within the groundwater at the PRB field site are measured to assess the water quality before

and after the treatment process. Groundwater samples were collected every month from observation wells and analysed for basic cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ), acidic cations (Al and total Fe), anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ), acidity and alkalinity.

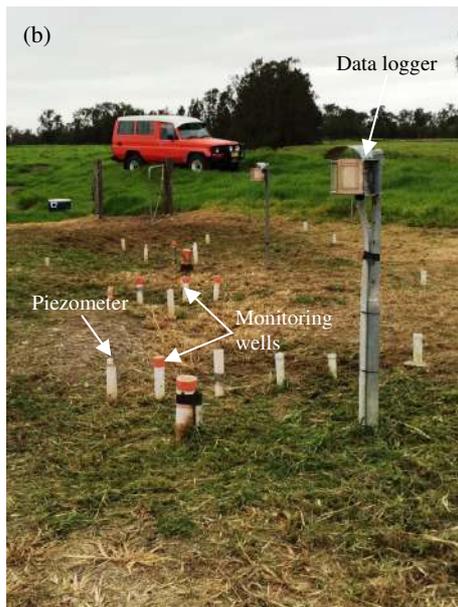


Figure 8 (a) Installation of the PRB (b) PRB study site with monitoring wells, piezometers and data logger

Figure 9 shows the pH profile up-gradient, within the PRB and down-gradient. There was a prominent increase in pH inside the PRB compared to that of the up-gradient. Groundwater inside the PRB has steadily been alkaline to neutral. This is quite a promising result, which has been stable till now (pH ranging from 10.2 to 7.2). This shows the recycled concrete particles' ability to neutralize the acidic groundwater via the dissolution of Ca-bearing cementitious materials within the recycled concrete aggregates and the release of carbonate alkalinity. However, changes in pH are highly dependent on dilution during heavy rainfall events and the flushing of acid during small rainfall events. There is a slight reduction in the down-gradient groundwater pH, which is probably due to the dilution of the PRB effluent by mixing with the untreated acidic groundwater. Although the PRB could remediate the acidic groundwater, it is not capable of reducing the pyrite oxidation process.

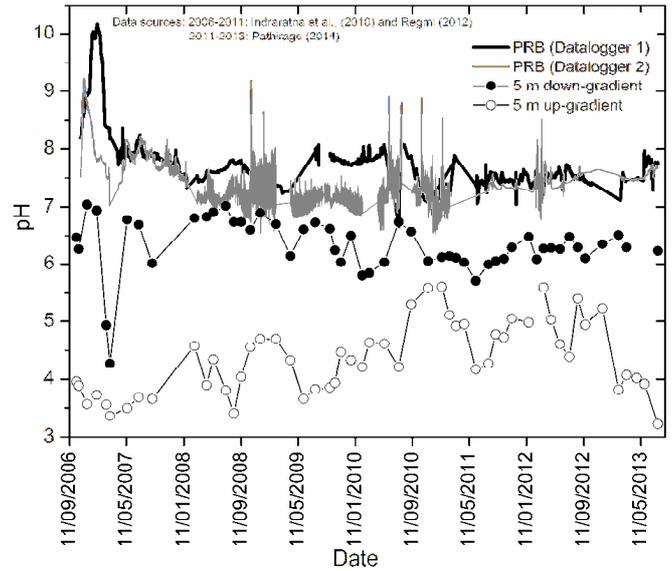


Figure 9 pH profiles at the up-gradient, PRB and down-gradient (after Indraratna et al. (2014a))

Moreover, high concentrations of dissolved Al and Fe were found in the up-gradient groundwater, fluctuating from 1.5-60 mg/L and 2-290 mg/L, respectively (Figure 10). The results showed that 95% of the dissolved Al and Fe in groundwater precipitated when alkaline minerals within recycled concrete dissolved. Minimal concentrations of Al and Total Fe were observed inside the PRB, which were less than 2 and 0.5 mg/L, respectively (Figure 10). The result indicates exceptional removal efficiency of the recycled concrete for Al and Fe. The amount of Al and Fe present in the up-gradient groundwater depends on rainy and drought seasons as well. As an example, during the rainy season followed by drought, groundwater will have more acidity and more Al and Fe concentrations subject to the oxidation of pyrite during drought season. Also, the amount of Al and Fe presence in groundwater depends on the availability of acid sulfate soils in that area, which is not distributed evenly in the field site.

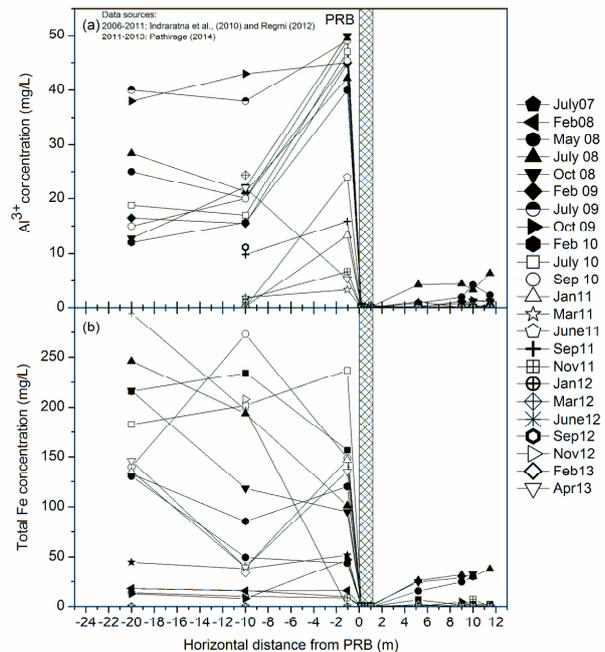


Figure 10 Dissolved (a) Al and (b) Fe concentrations at the up-gradient, PRB and down-gradient (after Indraratna et al. (2014a))

The concentrations of dissolved Al and Fe in the down-gradient groundwater slightly increased because of the active oxidation of pyrite and the liberation of these metals from the clay minerals in the soil down-gradient of the PRB and the mixing of alkaline effluent from the PRB with untreated acidic groundwater that is enriched with these acidic cations. Although the down-gradient concentrations were slightly higher than those inside the PRB, they were still higher than the up-gradient acidic groundwater.

Indraratna et al. (2014b) developed a coupled hydro-geochemical model to verify the performance of the PRB. A novel geochemical algorithm was developed listing all the dominant chemical reactions taking place between acidic groundwater and recycled concrete particles. MODFLOW and RT3D finite difference codes were used to numerically model the problem. The results have verified that the numerical solutions were in similar agreement with field observed data (Table 1).

Table 1 Model predicted and measured pH, Al and total Fe concentrations in the field PRB for 2012 (after Indraratna et al. (2014b))

	Input values	Averaged measured values inside the field PRB	Averaged model predicted values inside the field PRB
pH	3.6	7	7.3
[Al] (mg/L)	27	1	0.5
[Total Fe] (mg/L)	80	1	0

The results revealed that pH of the acidic groundwater were elevated to neutral pH while the high concentrations of dissolved Al and Fe have been precipitated out from the inflow solution. These precipitates have clogged the porous media and the calculated reduction in hydraulic conductivity of the PRB was 3% after running for six years. The small reduction in hydraulic conductivity was probably due to the coarse grained ( $d_{50} = 40$  mm) reactive media.

## 2.6 Longevity of PRB

The longevity the PRB depends on the exhaustion rate of reactive material and the precipitation rate of secondary minerals (Pathirage and Indraratna, 2015). The continuous secondary mineral precipitation over time would decrease the effectiveness of the PRB, because they clog the reactive surfaces of recycled concrete particles and consequently reduce the acid neutralisation capacity (ANC). The column experiments revealed that the reduction in ANC due to secondary mineral precipitation was 54%. This implies that the threat for long-term performance of the PRB would be the exhaustion of reactive material due to acid neutralisation and armouring of the reactive surfaces by secondary minerals. This pilot-scale PRB contained 80 tonnes of recycled concrete (ANC of 146 g/kg), from that at least 11.7 tonnes of acid neutralisation capacity was expected to be available in this PRB. With a mean groundwater flow velocity of 0.05 m/day and with an initial PRB porosity of 50%, acid transportation through the PRB was about  $4.85 \times 10^5$  L/year. The averaged acidity at the study site from September 2010 to July 2012 was 565 mg/L (equivalent to  $\text{CaCO}_3$ ), with a corresponding consumption of reactive material of 0.274 t/year. Therefore, in order to consume all the capable acid neutralising material, it would take 42.7 years ignoring the effect of armouring by secondary minerals precipitation. When the effect of secondary minerals precipitation on ANC was incorporated, (i.e. 54%), the estimated longevity of the PRB would be at least 19.5 years for a mean groundwater velocity of 0.05 m/day. Naturally, the computed longevity would vary according to the groundwater flow velocity and the respective consumption of reactive material (Pathirage and Indraratna, 2015).

## 3. CONCLUSION

This paper outlines the different treatment methods practiced in the Shoalhaven Floodplain, southeast NSW, Australia where acidic groundwater generation from ASS has been detrimental to the environment. V-notch weirs and self-regulating tilting weirs have been used to manipulate the groundwater table above the sulfidic soil horizon, thus minimising the oxidation of pyritic soil. The water table manipulation has proven to be successful in terms of maintaining the groundwater table, but was not promising for long-term application in low-lying flood prone areas. On the other hand, flood gates were quite effective in allowing tidal water to flow into the flood mitigation drains, thereby buffering the acidity before entering into the main waterways. Nevertheless, the efficacy of these modified floodgates were not enough especially during heavy rainfall events due to their inability to generate sufficient alkalinity to buffer the highly acidic drain water.

The lime-fly ash barrier has shown better performance in terms of raising the pH and reducing the dissolved Al and Fe in the groundwater, yet again was not promising as a long-term solution. In comparison to the abovementioned engineering solutions, the PRB has shown better performance since its installation in 2006. The groundwater pH has continuously been maintained near-neutral and the removal of dissolved Al and Fe from groundwater is 95%. However, PRB is not capable of reducing the pyrite oxidation process, as the barrier does not stop or reduce atmospheric oxygen from reaching the pyrite layer and causing pyrite oxidation. The pyrite oxidation process can only be maintained by sustaining the groundwater table above the pyritic layer via weirs and floodgates. On the other hand, the material cost and maintains cost are relatively negligible in PRB compared to other methods. Therefore, the authors propose that the use of a PRB to treat acidic groundwater in ASS terrain is more cost-effective, eco-friendly and promising in the long-term compared to previously utilised remediation methods

## 4. ACKNOWLEDGEMENT

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