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### Key strategies for managing acid sulphate soil (ASS) problems on the southeastern coast of New South Wales, Australia

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#### ABSTRACT

The acidification of Australian coastal waterways as a result of the oxidation of acid sulphate soil (ASS) containing appreciable quantities of sulphidic material (e.g. pyrite) has well recognised environmental, economic and social effects including the loss of fish, biodiversity and agricultural productivity as well as the corrosion of concrete and steel infrastructure by acidic drainage. Largescale artificial drainage and one-way floodgates in low-lying coastal floodplains has lowered the groundwater table, thus enhancing pyritic oxidation and increasing the distribution, magnitude and frequency of acid generation and release of toxic metals such as aluminium (Al<sup>3+</sup>) and iron (total Fe) from ASS. Engineering strategies implemented on the Shoalhaven Floodplain, southeast New South Wales, Australia have been designed to remediate ASS. These include: (1) fixed-level v-notch weirs, which raise the groundwater table above the pyritic layer and reduce the rate of discharge of acidic products from the groundwater into the drains; (2) modified two-way floodgates, which allow for tidal buffering of acidic drainage; (3) a subsurface alkaline horizontal impermeable lime-fly ash barrier, which prevents pyrite oxidation and neutralises acidic groundwater and (4) an alkaline permeable reactive barrier (PRB) using recycled materials, which significantly increases groundwater pH and reduces AI and Fe concentrations within and down-gradient of the PRB. A critical review of each of these strategies will outline their role in remediating ASS and their respective benefits and limitations.

*Keywords:* acid sulphate soil, groundwater manipulation, tidal buffering, neutralisation, permeable reactive barrier

#### 1 INTRODUCTION

Acid sulphate soil (ASS) has been widely recognised in coastal Australia since the 1960s with approx. 3 million ha of ASS identified with up to 0.6 million ha in New South Wales (NSW) alone (White et al. 1997). Chemical and bacterial oxidation of these soils, which contain appreciable amounts of sulphidic materials such as iron pyrite (FeS<sub>2</sub>), generates sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), which if not managed appropriately, drains into nearby waterways causing severe environmental, economic and social problems. This includes the acidification and contamination of soil, groundwater and surface water with dissolved aluminium (Al<sup>3+</sup>) and iron (Fe), massive fish and oyster kills (Indraratna et al. 2001) and the corrosion of concrete and steel infrastructures (e.g. foundations, floodgates, bridge piers, pipelines and culverts) (Sammut et al. 1996). Large-scale artificial drainage in low-lying coastal areas of Australia since the 1960s for the establishment of agricultural land has increased the distribution, magnitude and frequency of acid generation with acid discharge rates for drained agricultural land estimated to range from 100 to 500 kg H<sub>2</sub>SO<sub>4</sub>/ha.year (Blunden et al. 1997, Wilson et al. 1999).

Many traditional techniques for ASS remediation, such as drainage design and water table management (White et al. 1997, Johnston et al. 2004), are relatively ineffective in preventing continued oxidation of sulphidic materials unless severely reducing conditions are reinstated. Other techniques include capping, excavation and removal, bio-treatment and liming. Capping, involving the placement of an impermeable material over the sulphidic material to lower the rate of oxygen ( $O_2$ ) and water entering the soil, is ineffective as it does not prevent continued pyrite oxidation. The removal of pyritic materials is an aggressive, expensive and environmentally intrusive management option. Conventional lime neutralisation using calcium carbonate (CaCO<sub>3</sub>) or agricultural lime produces large volumes of metal-rich sludge (Benner et al. 1999) and the adoption of large-scale liming treatment is prohibitively expensive given the quantity of lime required to neutralise acidity in the soil.

Extensive research has been undertaken at the University of Wollongong on the development of effective and low-cost engineering strategies for the remediation of ASS in the Shoalhaven Floodplain, southeast NSW including fixed-level v-notch weirs, two-way modified floodgates, a subsurface alkaline lime-fly ash barrier and a permeable reactive barrier (PRB). This paper evaluates the effectiveness of these engineering strategies in remediating ASS.

#### 2 ACID SULPHATE SOIL REMEDIATION TECHNIQUES

#### 2.1 Study site locations

The remediation study sites are located within a small sub-catchment of approximately 120 ha located in ASS terrain (~2500 ha total high risk ASS) between the townships of Berry (34.7°S, 150.7°E) and Bomaderry (34.8°S, 150.6°E) in the Shoalhaven Floodplain, southeast NSW, Australia (Figure 1). This region is very low-lying with pyritic soil within close proximity to the surface organic layer. A network of flood mitigation drains (3.5 m deep × 8 m wide) were constructed across the sub-catchment in the late 1960s to minimise the risk of flooding on agricultural land. These drains discharge into Broughton Creek, a left bank tributary of the Shoalhaven River. One-way, top-hinged floodgates located at the entrance of most drains inhibit tidal intrusion of estuarine water, maintain low drain water elevations and lead to the build-up of acid reservoirs behind the floodgates. High levels of acidity, as indicated by massive acid scalds on the Shoalhaven Floodplain, create unfavourable conditions for vegetation growth, which directly affects local dairy farming and other forms of agriculture.



Figure 1. Map of study sites, Shoalhaven River floodplain, southeast NSW, Australia (shaded sections represent areas affected by acid sulphate soils) (Adapted from Indraratna et al. 2001)

#### 2.2 Groundwater manipulation via fixed-level v-notch weirs

The first ASS remediation strategy adopted within the Shoalhaven Floodplain was the implementation of fixed-level weirs in 1998, after numerical modelling showed the maintenance of the groundwater surface above the pyritic layer (1.2 m below ground surface, -0.3 m Australian Height Datum (AHD)) and a reduction in the amount of acid generated (Blunden and Indraratna 2000). Comprehensive field trials were implemented to verify improvement of ground and drain water at the field site by three v-notch weirs installed in flood mitigation drains (Indraratna et al. 2001). During the pre-weir period, drought periods characterised by high rates of evapotranspiration and low rainfall led to very low groundwater tables that exposed pyritic soil to oxidising conditions (Figure 2A). The v-notch weirs were successful in maintaining the groundwater table at or above the pyritic layer at most locations for the monitoring period (Figure 2B). The lower hydraulic gradients established under the influence of the higher drain water level maintained by the weirs reduced the discharge of acidic oxidation products from the groundwater to the drain. However, elevated groundwater levels did not improve the long-term groundwater quality with pH maintained at 3.5-4.0 throughout the monitoring period following weir installation. The weirs were able to reduce 'new' acid formation but biological oxidation of pyrite can occur even under submerged conditions. The concentration of Al<sup>3+</sup> in the groundwater remained high

in the post-weir period (0.1-40 mM; pre-weir: 0.1-70 mM) due to pyrite oxidation and the dissolution of aluminosilicate clays (Blunden 2000). The build-up of debris and the growth of weeds upstream and downstream of the weirs also caused the disturbance of steady-state flow conditions and increased the risk of flooding in these low-lying locations.



Figure 2. Average groundwater table height (A) before and (B) after weir installation (Adapted from Blunden (2000))

#### 2.3 Tidal buffering via two-way modified floodgates

The second ASS remediation strategy adopted was the modification of floodgates to allow ingress of brackish creek water to improve drain water quality by the buffering action of carbonates  $(CO_3^{2-})$ , and bicarbonates (HCO3) present in seawater. Since floodgates modifications would change the hydrodynamics of a drain, a number of concerns including the change in drain water quality due to tidal buffering and optimisation of the drain water level with tidal influx without overtopping the levee bank were addressed prior to installation of the floodgates. Tidal restoration in a flood mitigation drain and subsequent changes in drain water composition were simulated using a geographical information system (GIS) and ion-specific code written within PHREEQC and laboratory experiments, respectively. The simulations and laboratory results indicated that tidal buffering could improve drain water quality (Indraratna et al. 2005). Two styles of modified floodgates were installed in October 2000; (1) a winchoperated floodgate that lifts vertically, controlling the amount of water entering the drain, and (2) an automated Smart Gate system that permits tidal flushing based on real-time monitoring of water quality (e.g. pH, electrical conductivity (EC), dissolved oxygen (D) and temperature) up- and downflow of the gate. Prior to floodgate modifications, the average pH of the drain water was 4.32, while the average pH post-modification was 6.04 (Figure 3). Al<sup>3+</sup> decreased by > 50% from 11.3 mg/L to 4.38 mg/L. Similarly, total Fe decreased from an average of 23.1 mg/L to 10.3 mg/L. Tidal flushing (i) reduced the acid reservoir effect, (ii) increased drain water DO levels, (iii) enhanced fish passage, (iv) decreased exotic freshwater weeds and (v) recharged the phreatic zone during dry periods.



Figure 3.Drain water pH pre- and post-floodgate modifications (Adapted from Indraratna et al. (2005))

The effectiveness of this acid buffering approach is dependent on a number of complex factors including groundwater transport, acid product rates and estuarine flushing dynamics (Glamore and Indraratna 2004). Limitations of the modified floodgates included regular maintenance of the data loggers, clearing of debris and the cost of construction and installation due to the advanced nature of the technology utilised. Similar to the v-notch weirs, this technique is unable to remediate existing acidity stored within the soil and is not feasible in very low-lying areas subjected to flooding during significant rainfall events.

#### 2.4 Neutralisation via subsurface alkaline lime-fly ash barrier

The third ASS remediation strategy was the injection of a lime-fly ash slurry to form an impermeable barrier above the pyrite layer (1.2 m below ground surface, -0.24 m AHD) to halt infiltration of O<sub>2</sub> and neutralise groundwater acidity. Lime and fly ash were selected due to their ability to neutralise acidity and pozzolanic nature, respectively. Varying lime-fly ash ratios were tested to decide on the most appropriate viscosity and ratio of constituents to be used in preliminary injection trials (Indraratna et al. 2006), the results of which were used to alter the proposed barrier installation methods. Two weeks after the barrier was completed (June 2004), coring of the treated area confirmed the formation of a continuous layer (0.7 m below ground surface) that had sufficiently hardened to form the semiimpermeable barrier of thickness 100-130 mm. Changes in groundwater composition were monitored in a network of 31 observation wells at the study site to determine the barriers effectiveness. The barrier significantly improved groundwater quality. Groundwater pH increased from an average of 3.28 to between 4.5 and 5.5 (Figure 4) after installation of the barrier, with greater influence evident close to the barrier than further away. The concentration of pyritic oxidation products A<sup>3+</sup> (pre-barrier: 35.7 mg/L; post-barrier: 20.1 mg/L) and total Fe (pre-barrier: 67.6 mg/L; post-barrier: 37.0 mg/L) in the groundwater also, on average, decreased. The CI:SO<sup>2-</sup> ratio in the groundwater increased after the barrier was installed from 0.38 to 0.80, which confirmed that the barrier had successfully controlled pyrite oxidation in the soil. A comparison between the average groundwater table elevations before (0.23 m AHD) and after (0.17 m AHD) installation also indicated a perched water table, which would reduce the exposure of pyritic soil to atmospheric O<sub>2</sub>, reduce pyrite oxidation and the generation of acidic products. While the barrier is relatively inexpensive to install, it only has a localised impact on groundwater quality and, thus, limited applicability due to the large areas of land that contain ASS within the Shoalhaven Floodplain. The longevity of the barrier is also uncertain, as it will become ineffective due to armouring by AI or Fe precipitates or by the exhaustion of the neutralising capacity of the lime and fly ash.



Figure 4. Groundwater pH pre- and post-installation of lime-fly ash barrier (Adapted from Indraratna et al. (2006))

#### 2.5 Neutralisation via permeable reactive barrier

A permeable reactive barrier (PRB) was identified as a potential ASS remediation strategy in these low-lying areas, where weirs and floodgates are not suitable. While PRBs have been widely used for the remediation of contaminants such as chlorinated organic compounds, acid mine drainage, radionuclides and heavy metals (Phillips et al. 2000, Gu et al. 2002, Waybrant et al. 2002), only one PRB had been previously reported in ASS terrain with limestone under oxidising conditions (Waite et al. 2002). A pilot-scale PRB (17.7 m × 1.2 m × 3.0 m) using recycled concrete aggregate (40 mm diameter) to neutralise acidic groundwater was installed in ASS terrain at Manildra Group's

environmental farm near Bomaderry, southeast NSW in October 2006. Recycled concrete was recommended as the most suitable reactive material based on batch tests of 25 alkaline materials (Golab et al. 2006) and short-term column tests (Golab et al. 2009).

The PRB has successfully neutralised the acidic groundwater to ~ pH 7.3 (Figure 5A) and removed ~ 95% of  $A^{3^{+}}$  and total Fe (Indraratna et al. 2010). Up-gradient of the PRB, the groundwater is acidic (~ pH 3.4-5.6). The average pH down-gradient of the PRB is > 6.0 due to dilution of acidic water by alkaline effluent from the PRB. Groundwater inside the PRB is alkaline to neutral (pH 10.2-7.3), confirming the effectiveness of recycled concrete for neutralising acidic groundwater in ASS terrain. However, a decrease in the neutralisation of acidity and removal efficiencies of Al<sup>3+</sup> and total Fe over time indicates chemical armouring of the concrete and, thus, a decrease in PRB longevity. A long-term column experiment using recycled concrete was undertaken to determine the neutralisation reactions occurring within the PRB (Regmi et al. 2011). A synthetic acidic influent of constant flow rate 2.4 mL/min was used to simulate groundwater from the field site using the average value of contaminants measured over a 6-month monitoring period. The average porosity of the concrete was 0.52 (total pore volume (PV) was 534 mL). Three plateaus were observed (Figure 5B) and attributed to the: (1) dissolution of carbonate/bicarbonate alkalinity at pH 7.9-7.7 (40 < PVs < 155) followed by a gradual decrease to pH 6.5 (235 PVs); (2) re-dissolution of Al hydroxide precipitates at ~ pH 4 (300 < PVs < 500); and (3) re-dissolution of Fe oxyhydroxide precipitates at ~ pH 3 (> 500 PVs). Armouring of the recycled concrete aggregates, observed as white and orange precipitates within the column, resulted in a decrease in the actual acid neutralisation capacity (ANC) of the concrete (71 mg/g as CaCO<sub>3</sub>, 250 PVs) by ~50% compared to its theoretical ANC (145 mg/g as CaCO<sub>3</sub>, 510 PVs). Although a decrease in hydraulic conductivity within the column was observed due to chemical armouring, this would not be a major problem in the PRB due to the larger particle sizes used compared to the column experiment. Currently, steady piezometric head within the PRB indicates that chemical armouring has not yet affected groundwater flow within the PRB. Research is currently being undertaken to quantitatively assess changes in flow behaviour due to armouring/clogging in order to develop a time-dependent porous medium flow model combining particle retention and groundwater flow with chemical precipitation. This will be used to determine corresponding reductions in void space within the PRB, thereby analysing the interrelated effects of acidic flow induced clogging and PRB effectiveness.



Figure 5. (A) Groundwater pH up-gradient, inside and down-gradient of the PRB. (B) Column effluent pH, Al<sup>3+</sup>and total Fe as a function of pore volume (Adapted from Regmi et al. (2011))

#### 3 CONCLUSION

The remediation strategies implement in ASS terrain on the Shoalhaven Floodplain, southeast NSW, Australia play different roles in managing acidic groundwater. The lime-fly ash barrier is designed to prevent pyrite oxidation by stopping the downward movement of oxygen into the soil and regulate the generation of acidic groundwater before it occurs in ASS, whereas the v-notch weirs, two-way modified floodgates and PRB treat the acidity after it has been generated. Due to this, improvement in ground and surface water quality differs between these remediation measures. While the v-notch weirs are relatively inexpensive to install, they did not significantly improve the quality of the ground and drain water and are not feasible in very low-lying areas because they raise the risk of flooding during heavy rainfall events and pyrite oxidation occurs even under submerged conditions. The two-way modified floodgates were more effective than the v-notch weirs in treating the acidic ground and

drain water. However, they require regular maintenance and are not appropriate in very low-lying areas. The lime-fly ash barrier only offers a localised impact and its longevity is uncertain because, ultimately the barrier will become ineffective due to either armouring by Al- and Fe-bearing precipitates or by the exhaustion of the neutralisation capacity of the lime and fly ash. The best longer-term solution for these low-lying areas is the construction of a PRB that can neutralise the acidic groundwater before entering nearby waterways.

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