**EDITH COWAN
UNIVERSITY**
PERTH WESTERN AUSTRALIA
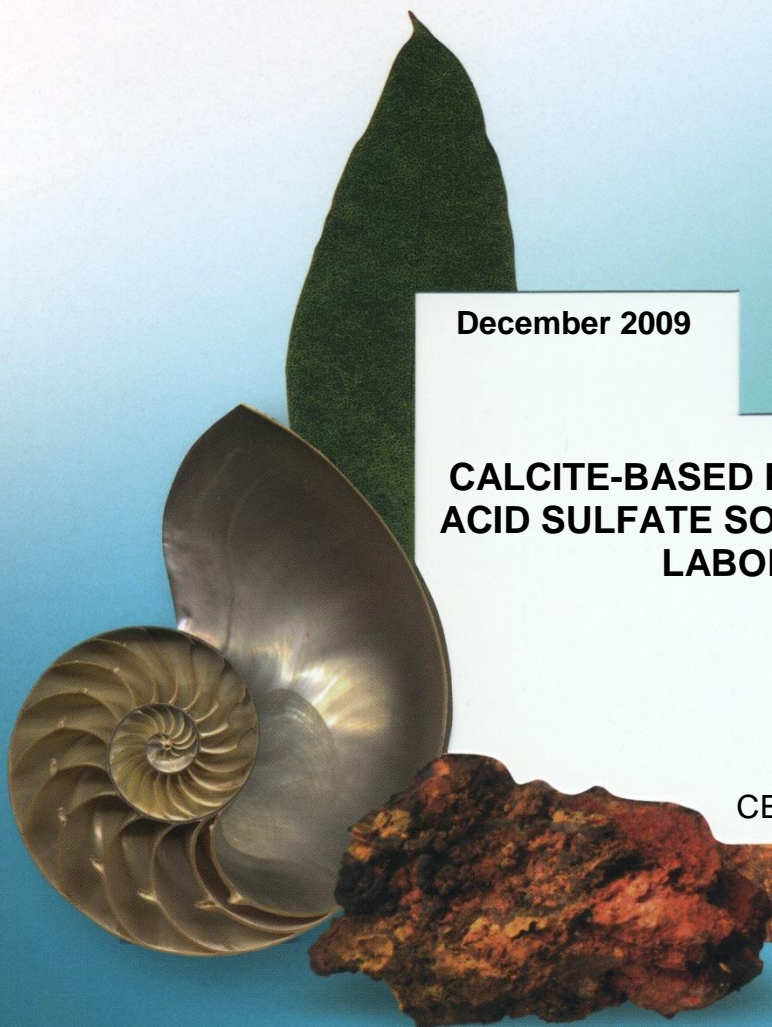
December 2009

CALCITE-BASED PELLET NEUTRALISATION OF ACID SULFATE SOIL WITHIN DELWANEY DRAIN: LABORATORY STUDIES

By, **Mr. Ryan Sawyer**
      Dr. Clint McCullough
      A/Prof. Mark Lund

December 2009

CALCITE-BASED PELLET NEUTRALISATION OF ACID SULFATE SOIL WITHIN DELWANEY DRAIN: LABORATORY STUDIES

By, **Mr. Ryan Sawyer**
Dr. Clint McCullough
A/Prof. Mark Lund

CEM Report No. 2009-04

Prepared for,

Water Corporation, Western Australia

Mr. Ryan Sawyer BSc (Hons), MSc Candidate,

Dr. Clint McCullough BSc, MSc (Hons), PhD (Aquatic Ecotoxicologist),

A/Prof. Mark Lund BSc (Hons), PhD (Aquatic Ecologist).

1. Executive Summary

1. Perth urban stormwater is channelled by drainage networks into local receiving water bodies. These drainage networks often include constructed wetlands intended for remediation of high stormwater nutrient and/or metal/metalloid concentrations.

2. Increased acidity and decreased pH associated with discharges from acid sulfate soils (ASS) may infiltrate stormwater drainage networks and impact constructed wetland water quality treatment processes.

3. Calcite-based ($CaCO_3$-based) pellets are produced during water purification at the Neerabup Groundwater Treatment Plant in Perth. Preliminary laboratory studies conducted by Water Corporation theorized these pellets were appropriate for neutralisation of acidic waters such as ASS discharges within stormwater drains.

4. Delwaney Drain and Brushfield Wetland are part of a stormwater drainage network within City of Stirling that is impacted by ASS contamination. Delwaney Drain was modified by Water Corporation to contain calcite-based pellets to neutralise ASS-related acidity entering the drain.

5. As discussed in CEM Report 2008-02, fieldwork at Delwaney Drain and Brushfield Wetland indicated that ASS contamination was present within Brushfield Wetland and the extent of contamination fluctuated dependent on the dominance of groundwater vs. stormwater influx. Sources of Brushfield Wetland acidity were likely Brushfield Wetland sediments and acidic groundwater inflow. The current application of calcite-based pellets in Delwaney Drain did not intercept highly ASS contaminated stormwater. Furthermore, physicochemical characteristics and ASS contamination indicators did not appear to vary between north and south sampling sites along the drain indicating insignificant water quality treatment prior to influx to Brushfield Wetland.

6. Theoretical neutralisation capacity of Water Corporation calcite-based pellets was investigated in the laboratory through acid neutralising capacity (ANC) and loss-on-ignition (LOI) analyses. ANC was conducted on both calcite-based and was $8.9 \pm 0.4\%$ $CaCO_3$. LOI results indicates calcite-based pellets had $17.1 \pm 4.0\%$ carbonate content. Such limited calcium carbonate content did not suggest the

calcite-based pellets would be a cost-effective acidity treatment strategy. If the maximum mean daily acidity from Brushfield Wetland occurred for the duration of that fieldwork, >6 times the volume of calcite-based pellets would have been required for acid neutralisation compared to pure calcium carbonate. Transport cost of calcite-based pellets may, therefore, outweigh the low material costs.

7. Column trials were conducted to evaluate acid neutralisation using calcite-based pellets with ASS contaminated water. Columns investigated both the impact of aeration vs. nitrogenation (i.e., aerobic vs. aerobic environments) and induced surface turbulence vs. vertical flow (i.e. surface turbulence over relatively stagnant water vs. water columns encouraged to mix).

8. Columns simulating surface water turbulence did not alter pH throughout the 10 d column study. Increases from $pH < 3$ to > 7 were observed in mixed columns irrespective of calcite-based pellet treatment or aeration/nitrogenation. These pH shifts were observed within approximately 2-4 days. Oxidation reduction potential (ORP) appeared to have an inverse relationship with pH in these columns.

9. Initial column water quality was consistent with previous analyses of Spoonbill-Shearwater Reserve. Neutralisation of acidity within mixed columns corresponded to decreased Al, Fe and NO_x, and increased $Cl:SO_4$ ratios. Water quality treatment was not observed in columns receiving solely surface turbulence.

10. Increased Ca was observed in all mixing columns with approximately 5 mg L^{-1} additional Ca in columns receiving calcite-based pellet treatment. As these columns all appeared to have increased pH, and increased Ca concentrations appeared relatively consistent (independent of calcite application), calcium carbonate dissolution was not likely responsible for acid neutralisation.

11. Bacterial sulfate reduction was evidenced by the formation of monosulfide black ooze (MBO) within mixed columns. This sulfate reduction was likely largely responsible for increased pH. The addition of mulch to all columns provided sufficient labile carbon for bacterial activity. While pH and ORP conditions may not have been optimal initially, SRB activity has been shown to occur under low pH conditions. Mixing likely assisted sulfate reduction by moving contaminated water to these optimal zones and/or promoting the expansion of such zones into the water column.

12. Decreased NO_x column concentrations may have also been related to bacterial activity as nitrate may be used as an electron acceptor within oxidizing conditions. Such nitrate reduction could have resulted in increased pH.

13. Presence of calcite-based pellets and treatment with aeration/nitrogenation did not appear to affect water quality treatment. Rather, flow within the water column (mixing vs. stagnant) appeared to be the sole factor influencing water quality treatment and acid neutralisation.

14. Calcite-based pellets produced by Water Corporation did not appear to be an effective material for neutralization of ASS discharges. Aluminium concentrations, however, appeared to be reduced with calcite-based pellet treatment. The use of the pellets for treatment of elevated Al concentrations could be researched further.

15. Increased pH in Brushfield Wetland during winter, therefore, may be due not only to dilution by uncontaminated stormwater, but also due to mixing induced by stormwater flows entering the Wetland. Further, there may be potential for simultaneous treatment of ASS discharges and urban stormwater containing contaminants including nitrate if proper conditions are established within wetlands, potentially through mixing.

Frontispiece

Delwaney Drain with calcite-based pellet application.

This document should be referenced as follows.

Sawyer, W. R. A., McCullough, C. D.; Lund, M. A. (2009). Calcite-based pellet neutralisation of acid sulfate soil within Delwaney Drain: laboratory studies. Centre for Ecosystem Management Report No. 2009-04, Edith Cowan University, Perth, Australia. 29 pp.

2. Contents

3. Background

Delwaney Drain is part of an urban stormwater drainage network with City of Stirling. The Drain discharges to Brushfield Wetland, a stormwater treatment wetland, which subsequently discharges to Lake Gwelup. Urban development has led to oxidation of potential acid sulfate soils (PASS) in the area and subsequent acidification of wetlands. Increased acidity was first identified in Stirling in the early-2000s (City of Stirling, 2006), which corresponds to a decrease in the Brushfield Wetland's pH to approximately pH 4 (D. Rajah, City of Stirling, personal communication, 2007).

As the area is known to be impacted by acid sulfate soil (ASS) discharges treatment strategies are necessary to consider. Development of low-cost materials and treatment strategies with minimal downstream environmental impacts is vital to treat areas affected by environmental acidification (Gómez del Río et al., 2004). Addition of acid-neutralising agents to acidic drainage is a common approach (Coulton et al., 2003). One such material is calcite ($CaCO_3$) which is typically used to adjust effluent pH to circumneutral, and optimize adsorption and precipitation of contaminants such as heavy metals (Sjöblom, 2003). Such techniques have been established with varying success or efficiency:

- Lime used as a slurry can act to neutralise acidity stored within ASS affected sediments/soils (Indraratna et al., 2006).
- Anoxic limestone drains generally work effectively to decrease acidity but the generation of hydroxide precipitates may decrease permeability of the drain and lead to system failure within as little as 6 months (Johnson & Hallberg, 2005).
- Treatment wetlands have become more efficient at treating acidic discharges following the inclusion of anoxic limestone drain systems in conjunction with existing wetlands (Kleinmann et al., 1998).

Wilson et al. (1999) have indicated that the direct application of calcite or other liming products to soil or waterways has the potential to assist in mitigating acidification caused by ASS. The amount of calcite remaining within treatment

systems decreases as acid neutralisation occurs (Caraballo et al., 2007). Such strategies, therefore, typically require human intervention, large amounts of neutralising agent and are not always cost-effective (Johnson & Hallberg, 2005; Palko & Weppling, 1995; White et al., 1997). Further, large amounts of sludge that are typically produced require disposal (Johnson & Hallberg, 2005).

Neutralisation of acidic waters from ASS occurs through the dissolution of calcite and its reaction with sulfuric acid resulting in decreased acid (H^+) (equation [1]) (Czop et al., 2007). Following this dissolution process, significant quantities of sulfide minerals are often found within sediments or treatment substrates due to microbial sulfate reduction by sulfate-reducing bacteria (SRB) (Czop et al., 2007). It has been demonstrated that sulfate reduction occurs in conditions $pH < 5$ within alkaline micro-environments (Koschorreck, 2008; Koschorreck et al., 2003; McCullough et al., 2008) despite Postgate's (1984) assertion that low ecosystem pH was severely limiting to SRB activity. SRB also require a source of organic carbon and it is vital that this organic carbon source is effective and economical (McCullough et al., 2008). As a result treatment systems are often developed containing reactive mixtures including organic material and a neutralising agent (Caraballo et al., 2007). One potential organic material that is often readily available is green waste such as mulch. Large reductions in sulfate concentrations and acidity within AMD have been observed following mulch treatment, particularly when combined with additional organic material such as sewage sludge (McCullough et al., 2006; Waybrant et al., 1998).

$$CaCO_3 + 2H^+ + SO_4^{2-} \rightarrow Ca^{2+} + H_2CO_3 + SO_4^{2-} \qquad [1]$$
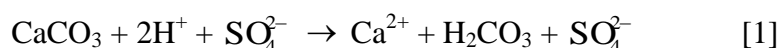
Calcite-based water quality treatment was established within Delwaney Drain by Water Corporation. This treatment strategy used calcite-based pellets produced during water purification processes with the aim of increasing alkalinity within stormwater prior to its discharge to Brushfield Wetland (Water Corporation, 2006). Field monitoring of the treatment application was unable to examine pellet efficacy due to limited continuous flow through Delwaney Drain and lack of acidity within influent stormwater (Sawyer et al., 2008). Therefore, laboratory analyses were required to examine ASS treatment efficacy with calcite-based pellets from Water Corporation. The pellets, already used for drinking water purification, were not pure calcium

carbonate as evidenced by their reddish colour. It remained unclear whether the pellets:

- had acid neutralising potential, particularly due to previous armouring, and,
- were appropriately placed in the Delwaney Drain to intercept ASS discharge (i.e., differences between flow-through and flow-over treatment strategies).

4. Methods

Calcite-based pellets were collected from the Water Corporation Neerabup Groundwater Treatment Plant. Ten replicate acid neutralising capacity (ANC) titrations were conducted for the calcite pellets following Ahern et al. (2004)'s Acid Reacted and Back-Titration method (19A2) (recorded results were taken as the mean of 3 titrations with results within 1% error).

Loss-on-ignition was determined using 40 g samples following drying at 105°C for 24 h and then burning at 550°C for 12 h to estimate organic carbon content. Carbonate content was then determined based on further weight loss following burning at 950°C for 12 h.

Laboratory column trials were conducted with 120 mm diameter, 600 mm long clear acrylic cores. The cores were plugged with rubber stoppers on the bottom and plastic lids allowing an input gas tube and small output vent capped the tops, and were contained within 50 L tubs filled with water to minimize pressure that may have caused leaks. Temperature was kept constant at 25°C throughout the trials and plastic tarps were used to limit direct sun. Columns received 100 g of mulch from the experimental ASS discharge treatment system at Spoonbill-Shearwater Reserve in City of Stirling as an organic carbon source as per Harmsworth et al. (2008). Mulch was added to the columns following the addition of water and calcite as appropriate for the treatments. As water from Delwaney Drain was not found to be acidic, acidic ASS contaminated water was collected from Spoonbill-Shearwater Reserve to compliment the source of mulch and previous ASS treatment research within City of Stirling. An apparatus was constructed using plastic disks which were perforated with a drill and 20 mm PVC tubing which was placed in the bottom of each core (Figure 1). Twelve columns were aerated to promote aerobic conditions while twelve columns were nitrogenated to promote anaerobic conditions. Within these treatments, six columns received gas through a hose at the bottom of the columns under the perforated disk to promote flow throughout the column, mixing and flow through calcite-based pellets if appropriate. The remaining six columns in each of the respective gas treatments received gas bubbles at the surface to simulate surface turbulence on a relatively stagnant drain or wetland. Finally half of these columns within each of these four treatments received 200 g of calcite-based pellets while the

remainder was untreated. In total there were eight treatments accounting for the presence of calcite-based pellets, aerobic vs. anaerobic conditions and water flow (stagnant vs. mixing). Acronyms used for identifying the columns are given in Table 1.

Table 1: Column descriptions and acronyms.

Column Acronym	Column Description
OBT	Aeration, Mixing
OBTC	Aeration, Mixing, Calcite-Based Pellets
NBT	Nitrogenation, Mixing
NBTC	Nitrogenation, Mixing, Calcite-Based Pellets
OBO	Aeration, Surface Turbulence
OBOC	Aeration, Surface Turbulence, Calcite-Based Pellets
NBO	Nitrogenation, Surface Turbulence
NBOC	Nitrogenation, Surface Turbulence, Calcite-Based Pellets

Physicochemical factors including pH, EC, ORP, DO and T were monitored daily at approximately 10:00 h using YSI 600XLM multiparameter sondes (YSI, USA). Water samples from each core prior to and after the trials were analysed for dissolved organic carbon (DOC), chloride (Cl^-), sulfate (SO_4^{2-}), calcium (Ca), iron (Fe), aluminum (Al), nitrate/nitrite (NO_x), ammonium (NH_4) and filterable reactive phosphorus (FRP).
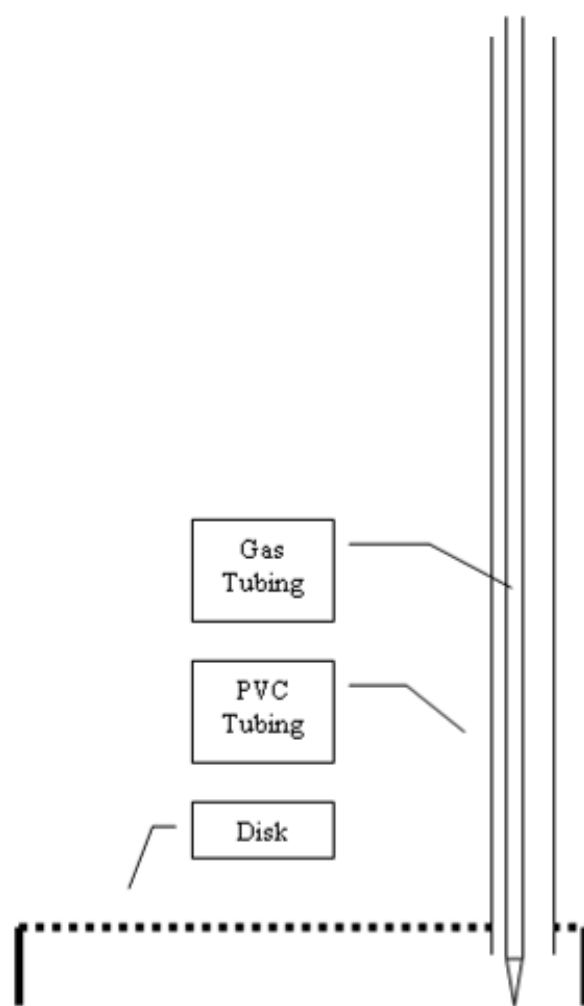
Figure 1: Apparatus at bottom of calcite trial cores.

5. Results & Discussion

Physicochemical conditions only changed within columns simulating mixing, in which water quality improvements were observed within approximately 2-4 days. Increased pH was observed from pH <3 to >7 (Figure 2). The NBT treatment did have some affect on pH, however not to the extent of the other mixed columns with a maximum pH of 4.5 reached throughout the study. A slight inverse pH vs. ORP reaction occurred with ORP declining as pH increased.
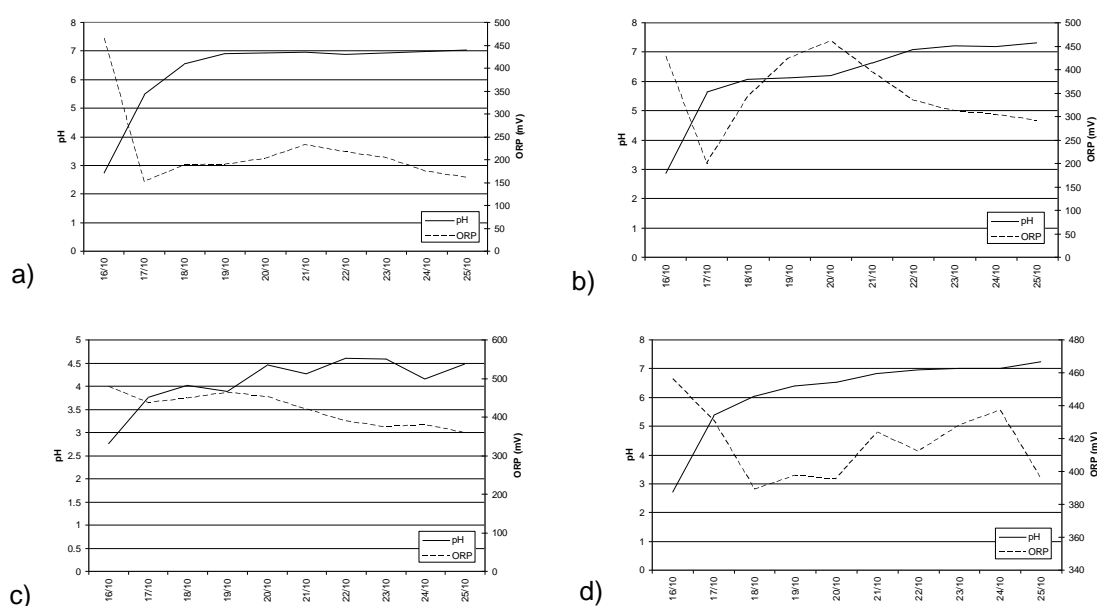

Figure 2: Mean pH and ORP data for column treatments OBT (a), OBTC (b), NBT (c) and NBTC (d).

DO concentrations in the mixed columns increased to near 100% within aerated columns, and < 20% within nitrogenated columns. Mulch treatment appeared to enhance the generation of anoxic conditions within nitrogenated columns, but did not limit aerobic conditions caused by aeration.

Similar to pH, chemical analyses of initial and final water samples indicated water quality treatment for various contaminants occurred solely within mixing columns. Al concentrations decreased in all mixed columns except NBOC (Figure 3). Initial mean Al concentration across the columns was 0.74 ± 0.01 mg L^{-1}. Concentrations of Al decreased to mean 0.22 ± 0.12 mg L^{-1} (70% decrease) within mixed columns while decreasing by only 20% in columns simulating surface turbulence.

Fe concentrations decreased similarly to Al in all columns except NBOC (Figure 4). At onset of experimentation the columns had mean Fe concentration of 25.1 ± 0.6 mg L^{-1}. Mean Fe concentrations decreased within surface turbulence columns by a maximum of approximately 4 mg L^{-1} (3%) while Fe reductions between 10-15 mg L^{-1} (approximately 48%) occurred in mixed columns.
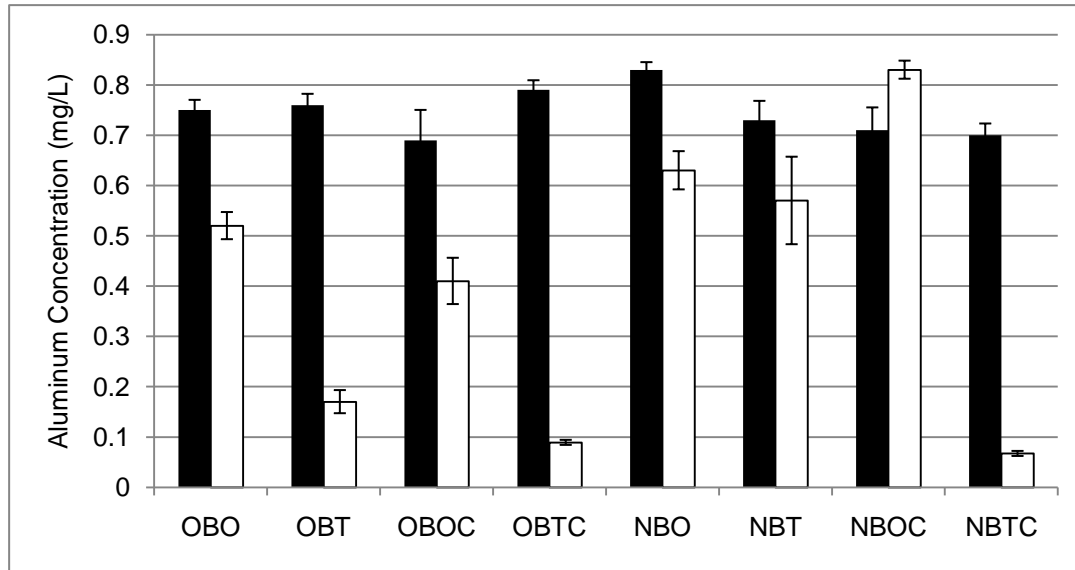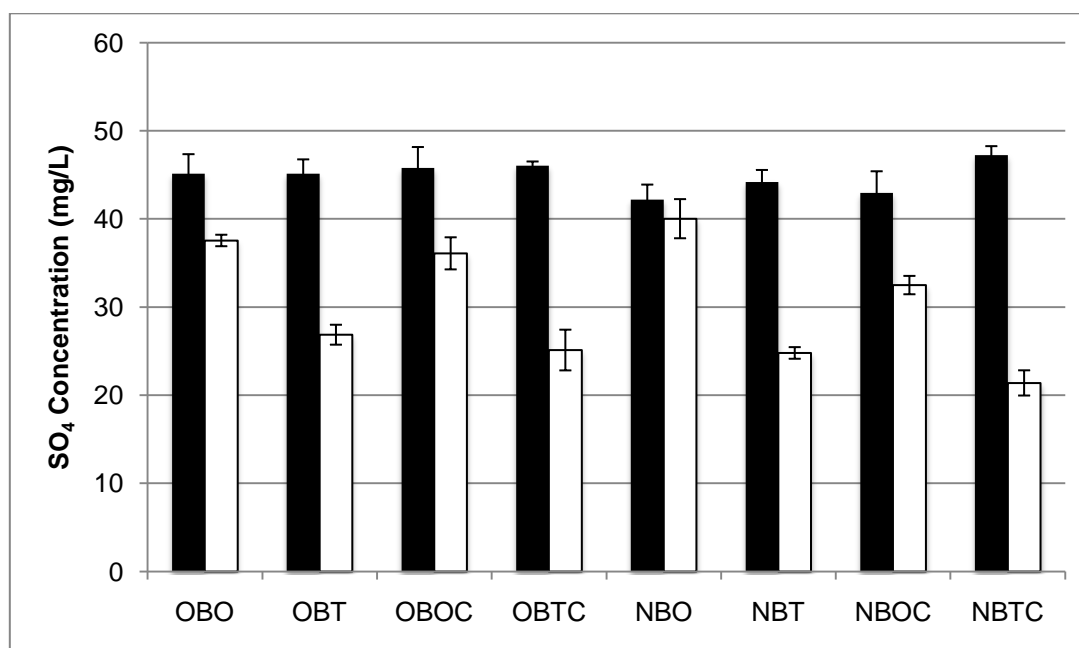

Figure 3: Initial (black) and final (white) Al concentrations from calcite-based pellet trials.
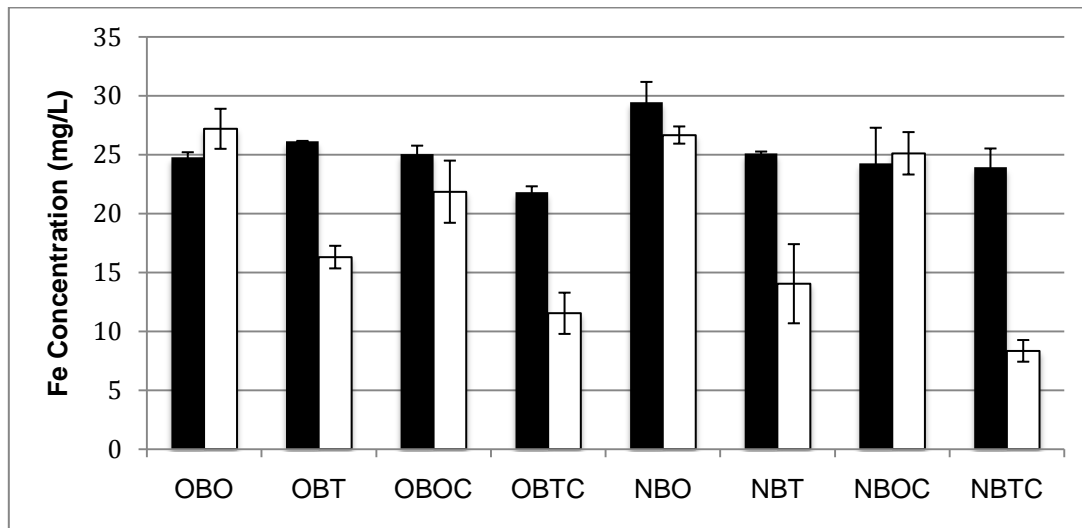
Figure 4: Initial (black) and final (white) Fe concentrations from calcite-based pellet trials.

Calcium concentration changes appeared independent of treatment. Mean initial Ca concentration within the columns was 50.6 ± 0.5 mg L^{-1}. Final mean Ca concentration was 52.2 ± 1.4 mg L^{-1}.

Sulfate had an initial mean concentration of 44.46 ± 0.62 mg L^{-1} (Figure 5). Surface turbulence columns had a mean 17% decrease in sulfate concentration. Substantially higher decreased sulfate concentrations (46% to 24.6 ± 1.1 mg L^{-1}) occurred within mixed columns. Chloride concentrations had similar responses in both flow treatments. Concentration decreases of 12% and 13% occurred in the surface turbulence and mixed columns respectively The mean initial chloride:sulfate (Cl:SO$_4$) ratio was 0.77 ± 0.02 (Figure 6). Within surface turbulence columns this ratio increased by an approximate mean of 6% while it increased by a mean 39% in mixed columns.

Figure 5: Initial (black) and final (white) sulfate concentrations from calcite-based pellet trials.
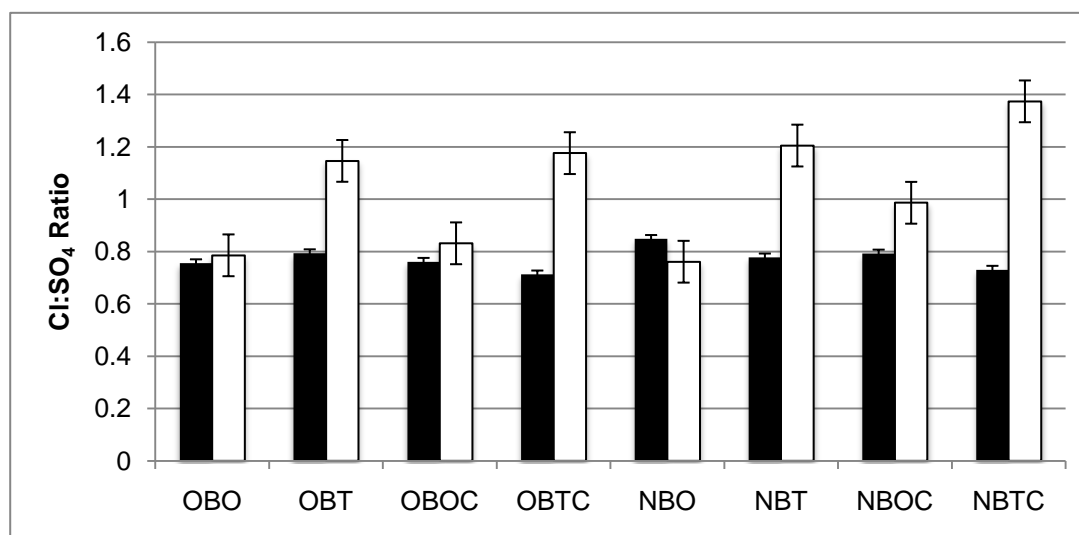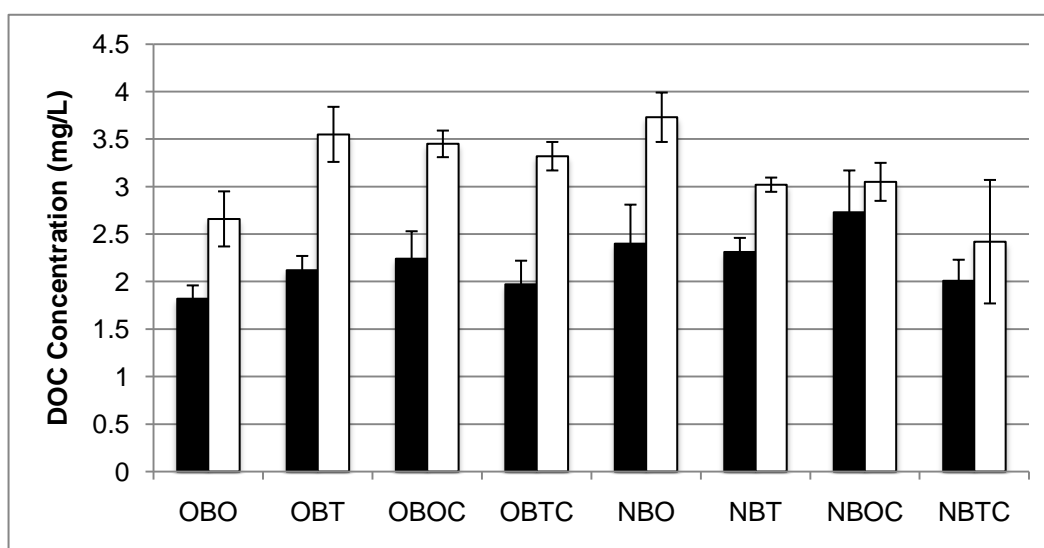
Figure 6: Initial (black) and final (white) Cl:SO$_4$ ratios from calcite-based pellet trials.

Filterable reactive phosphorus (FRP) had a mean initial concentration of $2.4 \pm 0.1 \ \mu g \ L^{-1}$. FRP concentrations decreased by mean 3% in surface turbulence and 6% in mixed columns. However, the large standard error of the mean suggested FRP fluctuations were not significant. These very low FRP concentrations were below ANZECC/ARMCANZ (2000) for freshwater south-western Australian wetlands ($<30 \ \mu g \ L^{-1}$).

Nitrate/nitrite concentrations were also all below the ANZECC/ARMCANZ (2000) water quality guideline of 100 μg/L. Initial concentrations were mean $41.3 \pm 0.4 \ \mu g \ L^{-1}$ Optimal treatment occurred within mixed columns with a mean percent decrease in NO$_x$ of 42%. Surface turbulence columns had a mean decrease in concentration of 8%. Ammonium concentrations appeared to increase within all columns, however, based on standard error significant increases were only observed within mixed columns. In all cases ammonium concentrations were above the southwestern Australian wetland ANZECC/ARMCANZ (2000) water quality guideline ($90 \ \mu g \ L^{-1}$). Initial ammonium concentrations were mean $262.0 \pm 1.1 \ \mu g \ L^{-1}$ and increased to final mean $265.7 \pm 0.9 \ \mu g \ L^{-1}$. Columns receiving surface turbulence had ammonium concentration increases of nearly 1%. Mixed columns had increased concentrations of approximately 2%.

DOC had mean initial concentration of 2.2 ± 0.10 mg L^{-1} (Figure 7). Concentrations of DOC increased irrespective of flow method (surface or mixed). Surface turbulence columns had a mean 29% increase and mixed columns had a 32% increase. DOC increases were likely caused by mulch additions.

Figure 7: Initial (black) and final (white) DOC concentrations from calcite-based pellet trials.

Within mixed columns little difference was observed between the columns treated with and without calcite-based pellets. The above figures show that Ca, Cl:SO$_4$, NO$_x$, and DOC concentration vary relatively consistently independent of calcite-based pellet presence. Slight increased Fe removal appeared to occur in columns containing calcite-based pellets, however standard error bars suggested this difference may be insignificant. Decreased Al concentrations, however, may be greater within columns containing calcite-based pellets, although Al concentrations within columns without calcite-based pellets were highly varied (Figure 8).
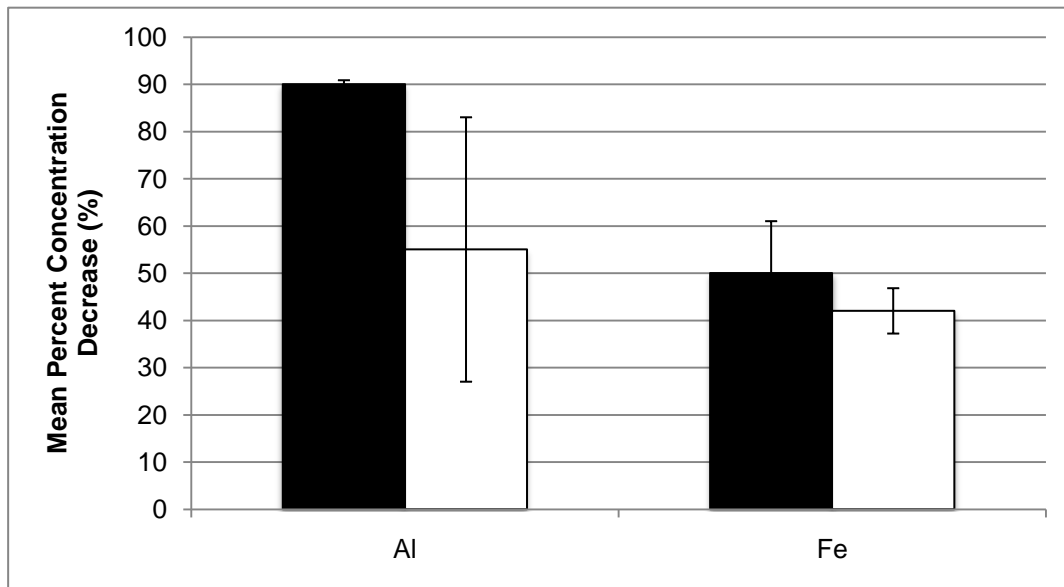
Figure 8: Mean percent decrease of Al and Fe concentrations within flow through columns containing calcite-based pellets (black) and without calcite-based pellets (white).

Initial water quality of Spoonbill-Shearwater Reserve water discussed above appeared consistent with previous studies (i.e. Harmsworth et al., 2008; Somesan et al., 2008) Neutralisation of acidity was observed within mixed columns rapidly, within 2-4 days. Improved water quality was also indicated by decreased Al, Fe and NO_x, and increased $Cl:SO_4$ ratios. Columns receiving minimal flow with solely surface turbulence, however, did not impact concentrations of ASS or urban stormwater contaminants. Overall, water quality treatment was observed in all mixed columns, and appeared independent of both oxygenated vs. deoxygenated environments and presence of calcite-based pellets. Increased $Cl:SO_4$ ratios in mixed columns showed increased ASS treatment due to mixing rather than due to calcite-based neutralisation.

Overall, increased Ca concentrations were observed in all columns. The difference in concentration increases between mixed columns with and without calcite-based pellet treatment was relatively minor (approximately 5 mg L^{-1}). All Ca concentrations were within ranges of previously observed wetlands within the region of the Swan Coast Plain (i.e. Kinnear & Garnett, 1999). As discussed above dissolution of calcium carbonate may lead to decreased H^+ acidity within water bodies (equation [2]) (Czop et al., 2007). As the calcite-based pellets had $< 10\%$ $CaCO_3$ equivalent acid neutralising capacity and did not appear to significantly change Ca concentrations it is

likely calcium carbonate dissolution was not responsible for decreased acidity or minor Ca concentration fluctuations within the columns.

$$CaCO_3 + 2H^+ + SO_4^{2-} \rightarrow Ca^{2+} + H_2CO_3 + SO_4^{2-} \qquad [2]$$
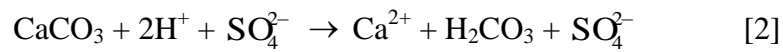
Alkalinity generation and increased pH, therefore, were likely caused by bacterial activity rather than calcite-based pellet chemical neutralisation. Such sulfate-reducing bacterial activity is primarily limited by the availability of labile organic carbon as acidic drainage typically has low DOC concentrations and SRB are particularly sensitive to organic carbon concentrations (Kolmert & Johnson, 2001; Liu et al., 2003; Neculita et al., 2007; Zagury et al., 2006). The addition of mulch likely provided the required organic carbon as DOC increases were consistently observed throughout the columns.

Bacterial sulfate reduction produces hydrogen sulfide (H_2S) as described by equation [3], which can then be transformed into sulfide minerals (Lucassen et al., 2002). Sulfate reduction and sulfide mineral formation was evidenced by the formation of monosulfide black ooze (MBO) at the bottom of mixed columns. MBO forms in drains with readily available labile carbon and reducing conditions (Fitzpatrick et al., 2005). Labile carbon was available due to increasing DOC in all columns, however, ORP was primarily oxidizing with a minimum of >150 mV. SRB activity has been thought to occur primarily within conditions with ORP < -100 mV and is inhibited by high ORP (Postgate, 1984). Similar to SRB activity that has been shown within low pH conditions (Koschorreck, 2008; Koschorreck et al., 2003; McCullough et al., 2008), which was previously considered extremely limiting (Postgate, 1984), reducing microenvironments have been observed leading to sulfate-reduction in localized zones within overall oxidizing environments (Brown et al., 1999; Jørgensen & Bak, 1991; Reisman et al., 2003). Reducing zones may, therefore, have allowed stable SRB activity and MBO formation within the generally oxidizing water columns (Reisman et al., 2003; Zaluski et al., 2003).

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad [3]$$
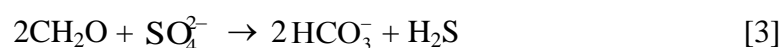
The formation of MBO through such processes, however, is not an effective method of treating ASS discharge within stormwater drainage. MBO may be re-oxidized releasing acidity and leading to severe deoxygenation of water bodies within flowing

drains (Sullivan et al., 2002). Upon drying of open drains, such as occurred regularly within Delwaney Drain, MBO has the potential to rapidly oxidize and lead to acidification upon re-wetting (as observed for Brushfield Wetland sediments) (Fitzpatrick et al., 2005). It is vital that such a by-product of ASS neutralisation be contained within the treatment system to avoid negative downstream effects within natural environments. Additionally, additional decreases in sulfate concentrations may have related to decreased Al concentrations and the formation of aqueous aluminium-sulfate complexes, however, such complexes are readily soluble and not a viable treatment option (Rose & Ghazi, 1998).

Bacterial activity and ORP also were likely key factors in decreasing nitrate concentrations within the columns. SRB within oxidizing conditions may decrease NO_x concentrations. Nitrate may be used by SRB as an electron acceptor for respiration within oxidizing conditions, producing ammonium (Boopathy et al., 2002; McCready et al., 1983). Nitrate reduction, therefore, may also be used within treatment systems to promote increased pH through the use of hydrogen ions and production of hydroxide ions as per equation [4] (Till et al., 1998). Low observed ammonium production may have resulted from a lack of sediments typically required for this process (Faulkner & Richardson, 1989). Further, mixing of wetland water is known to volatize ammonium leading to decreased aqueous concentrations (Kadlec & Knight, 1996). Nitrification of ammonium, however, is necessary to consider for water quality as all samples had concentrations in excess of the guideline value (ANZECC/ARMCANZ, 2000). Overall, mixing appeared to increase the production of ammonium and decrease nitrate concentrations. Such nitrate reduction corresponded to increased pH and may indicate potential use of nitrate reduction for remediation of ASS discharges.

$$2\,NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- \qquad [4]$$
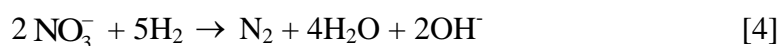
Water quality improvements and acid neutralisation, therefore, appeared to be due sulfate reduction by SRB with sufficient labile organic carbon due to mulch addition and the presence of consistent mixing throughout the water column promoting ideal conditions within micro-environments.

6. Conclusions

There is potential for acid neutralizing material to be placed within input or output drains of existing ASS contaminated urban stormwater treatment constructed wetlands to promote ASS treatment of contaminated water within stormwater drainage networks prior to discharge into receiving environments. However, the calcite-based by-products from Water Corporation appeared to have relatively low carbonate content and consequent neutralising capacity. Further, laboratory trials of the pellets demonstrated that calcite-based pellets produced during water purification processes did not inhibit or enhance treatment of either acidity, iron or sulfate. As such the pellets were likely unsuitable for the proposed treatment strategy at Delwaney Drain and Brushfield Wetland or elsewhere.

Cost-effectiveness would also be a vital consideration for environmental managers if alternative calcite-based pellet applications were investigated and found to assist in acidic water quality treatment. Approximately 11-12 units of Water Corporation calcite-base pellets would be required for every 1 unit of pure calcium carbonate, since the pellets had mean ANC = 8.9% $CaCO_3$ equivalent. Within Brushfield Wetland maximum acidity detected was 22 mg $CaCO_3 L^{-1}$. Should this have been the constant acidity over the entire study period total effluent acidity from the Wetland would have been approximately 555 kg $CaCO_3$ (based on the calculated 25,250,000 L outflow). Therefore, approximately 6,110-6,666 kg of Water Corporation calcite-based pellets would have been required over 5 months. Assuming pure calcium carbonate or lime to have an approximate cost of \$50/tonne (as per Bruce et al., 2000) the required 0.5 tonnes of pure reactive materials could be used for low cost (<\$50 outside of transport costs). Alternatively free calcite-based pellets may have large transport costs due to the large required volume (>6 tonnes).

The primary factor impacting water quality treatment was movement of water throughout the water column. As discussed, SRB activity appeared to occur within non-ideal environments including acidic waters with isolated alkaline microenvironments (Koschorreck et al., 2003; Praharaj & Fortin, 2004) and localized reducing zones in oxidizing conditions (Kolmert & Johnson, 2001; Reisman et al., 2003; Zaluski et al., 2003). Moreover, nitrate reduction may have assisted in

increasing pH (Till et al., 1998). It is, therefore, postulated that synthesized mixing may assist acidic water quality treatment within stormwater drainage networks and treatment wetlands by:

- forcing expansion of alkaline and/or reducing microenvironments with active SRB throughout the water column, and/or,
- causing sulfate to contact microenvironments with optimal conditions for SRB activity leading to treatment of ASS affected water, and/or,
- causing nitrate to contact microenvironments with optimal nitrate reducing conditions that are known to increase pH (Till et al., 1998).

Acidity treatment, therefore, may be enhanced compared to stagnant water bodies in which these microenvironments remain isolated. This supports Kadlec's (1994) assertion that water movement throughout constructed wetlands is vital for water quality treatment and mixing may be a key component as have been found for various contaminants. Calcite-based pellets produced by Water Corporation during water purification, however, did not appear to assist in neutralization of acidity associated with ASS discharges.

7. Recommended Future Work

1. Investigations into strategies for encouraging mixing within stormwater drainage networks and treatment wetlands may enhance acid sulfate soil (ASS) discharge water quality treatment. Moreover the extent of mixing within the water column may have optimal limits or ranges that require examination.

2. If inexpensive options could be established to de-armour calcite-based pellets from Water Corporation, research would be required to determine if the "clean" pellets were appropriate for ASS neutralisation. Alternatively, as the pellets did not appear to adversely impact water quality there may be potential for use as a substrate in a different application. For example, treatment of elevated Al concentrations may be possible with the pellets. However, this theory requires further research as this study do not quantify long-term effects of the pellets and/or long-term armouring potential.

3. It seemed clear water flowing over reactive media rather than mixing through reactive media was not effectively treated for acidity and ASS contamination. Strategies for stormwater drainage network ASS treatment should, therefore, focus on permeable reactive media. For example, reactive barriers within stormwater infrastructures such as the drain discharging to Brushfield Wetland.

4. Monosulfide black ooze (MBO) formed during acidity treatment and upon drying of environments such as wetlands and drains would have become a source of acidity. Strategies to contain MBO and/or remove MBO following water treatment should be investigated. This may also be necessary if large quantities of iron sulfide minerals are produced and oxidized within dried environments.

5. It appeared urban stormwater contaminated by nitrate and intercepting ASS discharges may potentially be treated simultaneously within mixed water columns. Further research may provide insight into combined treatment of such contaminants within coastal urban environments.

8. REFERENCES

Ahern, C. R., McElnea, A. E., Sullivan, L. A., & Water, D. o. (2004). *Acid Sulfate Soils Laboratory Methods Guidelines* (2.1 ed.). Indooroopilly, QLD, Australia: Queensland Government.

ANZECC/ARMCANZ. (2000). *Australian and New Zealand guidelines for fresh and marine water quality.* (National Water Quality Management Strategy Paper No. 4). Canberra, ACT, Australia: Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

Boopathy, R., Robichaux, M., LaFont, D., & Howell, M. (2002). Activity of sulfate-reducing bacteria in huan peridontal pocket. *Canadian Journal of Microbiology, 48*(12), 1099-1103.

Brown, C. J., Coates, J. D., & Schoonen, M. A. A. (1999). Localized sulfate-reducing zones in a coastal plain aquifer. *Ground Water, 37*(4), 505-516.

Bruce, R. C., Johnston, M., & Rayment, G. E. (2000). *Environmental Short Course for Sustainable Sugar Production*. Townsville, QLD, Australia: CRC for Sustainable Sugar Production.

Caraballo, M. A., Rötting, T., Nieto, J. M., & Ayora, C. (2007). *Mineralogical characterization of a reactive tank in a passive AMD treatment system at Monte Romero (Iberian Pyrite Belt, SW Spain).* Proceedings of the IMWA Symposium 2007: Water in Mining Environments, Cagliari, Italy:

City of Stirling. (2006). Lake Gwelup Reserve Management Plan. In *Agenda of the Infrastructure and Community Development Committee Meeting of 25 July 2006* (pp. 138-147). Stirling, WA, Australia: City of Stirling.

Coulton, R., Bullen, C., & Hallet, C. (2003). The design and optimization of active mine water treatment plants. *Land Contamination and Reclamation, 11*, 273-279.

Czop, M., Motyka, J., & Szuwarzyński. (2007). *Environmental impact of the AMD buffering process on groundwater quality in the Trzebionka zinc-lead mine vicinity (South Poland).* Proceedings of the IMWA Symposium 2007: Water in Mining Environments, Cagliari, Italy:

Faulkner, S. P., & Richardson, C. J. (1989). Physical and Chemical Characteristics of Freshwater Wetland Soils. In D. A. Hammer (Ed.), *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural* (pp. 41-72). Chelsea, MI, USA: Lewis Publishers, Inc.

Fitzpatrick, R. W., Baker, A. K. M., Raven, M., Rogers, S., Degens, B., George, R., et al. (2005). Mineralogy, biogeochemistry, hydro-pedology and risk of sediments, salt efflorescences and soils in open drains in the wheatbelt of Western Australia. In I. C. Roach (Ed.), *Regolith 2005* (pp. 97-101). Adelaide, SA, Australia: CRC LEME.

Gómez del Río, J. A., Morando, P. J., & Cicerone, D. S. (2004). Natural materials for treatment of industrial effluents: comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite. Part I: batch experiments. *Journal of Environmental Management, 71*, 169-177.

Harmsworth, K., McCullough, C. D., & Lund, M. A. (2008). *Does mulching improve water quality in an acid sulfate soil affected lake?* (Centre for Ecosystem Management Report No. 2008-07). Perth, WA, Australia: Edith Cowan University. Unpublished report to City of Stirling.

Indraratna, B., Golab, A. N., & Banasiak, L. J. (2006). Installation of a lime injection barrier for the remediation of acid sulphate soil problems. *Quarterly Journal of Engineering Geology and Hydrogeology, 39*(4), 391-401.

Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review. *Science of the Total Environment, 338*, 3-14.

Jørgensen, B. B., & Bak, F. (1991). Pathways and microbiology of thiosulfate transformations and sulfate reduction in a marine sediment (Kattegat, Denmark). *Applied and Environmental Microbiology, 57*(3), 847-856.

Kadlec, R. H. (1994). Detention and mixing in free water wetlands. *Ecological Engineering, 3*, 345-380.

Kadlec, R. H., & Knight, R. L. (1996). *Treatment Wetlands: Theory and Implementation*. Boca Raton, FL, USA: CRC Press.

Kinnear, A., & Garnett, P. (1999). Water chemistry of the wetlands of the Yellagonga Regional Park, Western Australia. *Journal of the Royal Society of Western Australia, 82*, 79-85.

Kleinmann, R. L. P., Hedin, R. S., & Nairn, R. W. (1998). Treatment of mine drainage by anoxic limestone drains and constructed wetlands. In A. Geller, H. Klapper & W. Salomons (Eds.), *Acidic Mining Lakes: Acid Mine Drainage, Limnology and Reclamation* (pp. 303-319). Berlin, Germany: Springer Publishing.

Kolmert, A., & Johnson, D. B. (2001). Remediation of acidic waste waters using immobilized, acidophilic sulfate-reducing bacteria. *Journal of Chemical Technology and Biotechnology, 76*, 836-843.

Koschorreck, M. (2008). Microbial sulfate reduction at a low pH. *FEMS Microbiolog Ecology, 64*(3), 329-342.

Koschorreck, M., Wendt-Potthoff, K., & Geller, W. (2003). Microbial sulfate reduction at low pH in sediments of an acidic lake in Argentina. *Environmental Science and Technology, 37*(6), 1159-1162.

Liu, X., Bagwell, C. E., Wu, L., Devol, A. H., & Zhou, J. (2003). Molecular diversity of sulfate-reducing bacteria from two different continental margin habitats. *Applied and Environmental Microbiology, 69*(10), 6073-6081.

Lucassen, E. C. H. E. T., Smolders, A. J. P., & Roelofs, J. G. M. (2002). Potential sensitivity of mires to drougt, acidification and mobilisation of heavy metals: the sediment S/(Ca+Mg) ratio as diagnostic tool. *Environmental Pollution, 120*, 635-646.

McCready, R. G. L., Gould, W. D., & Cook, F. D. (1983). Respiratory nitrate reduction by *Desulfovibrio* sp. *Archives of Microbiology, 135*(3), 182-185.

McCullough, C. D., Lund, M. A., & May, J. A. (2006). *Microcosm testing of municipal sewage and green waste for full-scale remediation of an acid coal pit lake, in semi-arid tropical Australia.* Proceedings of the 7th ICARD, St. Louis, MO, USA: 1177-1197.

McCullough, C. D., Lund, M. A., & May, J. A. (2008). Field-scale demonstration of the potential for sewage to remediate acidic mine waters. *Mine Water and the Environment, 27*(1), 31-39.

Neculita, C.-M., Zagury, G. J., & Bussière, B. (2007). Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: Critical review and research needs. *Journal of Environmental Quality, 36*, 1-16.

Palko, J., & Weppling, K. (1995). Modelling the effects of acid sulfate soils on river acidity in Finland. *Nordic Hydrology, 26*, 37-54.

Postgate, J. R. (1984). *The sulphate-reducing bacteria*. New York, NY, USA: Cambridge University Press.

Praharaj, T., & Fortin, D. (2004). Indicators of microbial sulfate reduction in acidic sulfide-rich mine tailings. *Geomicrobiology Journal, 21*(7), 457-467.

Reisman, D. J., Gusek, J. J., & Bishop, M. (2003). *A pre-treatability study to provide data for construction of a demonstration bioreactor.* Proceedings of the 10th International Conference on Tailings and Mine Waste, Vail, CO, USA: 305-315.

Rose, S., & Ghazi, A. M. (1998). Experimental study of the stability of metals associated with iron oxyhydroxides precipitated in acid mine drainage. *Environmental Geology, 36*(3-4), 364-370.

Sawyer, W. R. A., McCullough, C. D., & Lund, M. A. (2008). *Analysis of Delwaney Drain acid sulfate soil treatment using calcite pellets* (Centre for Ecosystem Management Report No. 2008-02). Perth, WA, Australia: Edith Cowan University.

Sjöblom, Å. (2003). *Wetlands as a Means to Reduce the Environmental Impact of Mine Drainage Waters*. Linköping, Sweden: Linköping University.

Somesan, N., McCullough, C. D., & Lund, M. A. (2008). *Riparian mulching as remediation of an urban acid sulfate soil (ASS) affected wetland* (Centre for Ecosystem Management Report No. 2008-19). Perth, WA, Australia: Edith Cowan University.

Sullivan, L. A., Bush, R. T., & Fyfe, D. M. (2002). Acid sulfate soil drain ooze: Distribution, behaviour and implications for acidification and deoxygenation of waterways. In C. Lin, M. D. Melville & L. A. Sullivan (Eds.), *Acid sulfate soils in Australia and China* (pp. 91-99). Beijing, China: Science Press.

Till, B. A., Weathers, L. J., & Alvarez, P. J. J. (1998). Fe(0)-Supported Autotrophic Denitrification. *Environmental Science and Technology, 32*, 634-639.

Water Corporation. (2006). *Water Quality Monitoring for the Trial Application of Calcium Calcite at Delwaney Branch Drain*. Perth, WA, Australia: Water Corporation.

Waybrant, K. R., Blowes, D. W., & Ptacek, C. J. (1998). Selection of reactive mixtures for use in permeable reactive walls for treatment of mine drainage. *Environmental Science and Technology, 32*(13), 1972-1979.

White, I., Melville, M. D., Wilson, B. P., & Sammut, J. (1997). Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management, 5*, 55-72.

Wilson, B. P., White, I., & Melville, M. D. (1999). Floodplain hydrology, acid discharge and change in water quality associated with a drained acid sulfate soil. *Marine and Freshwater Research, 50*, 149-157.

Zagury, G. J., Kulnieks, V., & Neculita, C. M. (2006). Characterization and reactivity assessment of organic substrates for sulfate-reducing bacteria in acid mine drainage treatment. *Chemosphere, 64*, 944-954.

Zaluski, M. H., Trudnowski, J. M., Harrington-Baker, M. A., & Bless, D. R. (2003). *Post-mortem findings on the performance of engineered SRB field-bioreactors for acid mine drainage control.* Proceedings of the 6th International Conference on Acid Rock Drainage, Cairns, QLD, Australia: 845-853.