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A SYNOPSIS OF POTENTIAL AMENDMENTS AND TECHNIQUES FOR THE NEUTRALIZATION OF ACIDIC DRAINAGE WATERS IN THE WESTERN AUSTRALIAN WHEATBELT

Grant Douglas and Brad Degens

CRC LEME OPEN FILE REPORT 209
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A technical report prepared for the Engineering Evaluation Initiative (EEI) and the Wheatbelt Drainage Evaluation Project, both commissioned as part of the National Action Plan for Salinity and Water Quality (NAPSWQ).

CRC LEME is an unincorporated joint venture between CSIRO-Exploration & Mining, and Land & Water, The Australian National University, Curtin University of Technology, University of Adelaide, Geoscience Australia, Primary Industries and Resources SA, NSW Department of Primary Industries and Minerals Council of Australia, established and supported under the Australian Government's Cooperative Research Centres Program.

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1 INTRODUCTION

Salinised land in the wheatbelt of Western Australia (WA) contained within the Avon River Basin (Figure 1) is expected to increase to over 3 million hectares (Clarke *et al*., 2002) unless the climate continues to be dry further slowing rates of groundwater rise. Mixed success with using vegetation based options to manage salinity in many parts of the WA wheatbelt has resulted in increased emphasis on the use of engineering options to counter rising saline groundwaters (Clarke *et al*., 2002). The main engineering option of choice for many wheatbelt valleys has been the use of deep (2-3m) open drains, which are increasingly being used to protect low-lying land from salinisation and rehabilitate marginally saline lands (Ali *et al*., 2004a, Dogramaci and Degens 2003). Over 10 000 kilometres of deep drains have already been constructed in parts of the WA wheatbelt with few regional linkages (Ali *et al*., 2004a). There is increasing interest amongst some valley farmers in the WA wheatbelt to increase the scale of these drainage systems and link smaller farm scale systems into larger regional drainage schemes (100's km in length covering 1000's km^2). In considering the feasibility of this scale of drainage, landholders, community and local government authorities have raised concerns about the possibility of increased flooding and water quality impacts occurring at landscape scales arising from such drainage schemes. These concerns are being addressed in WA by the Engineering Evaluation Initiative (EEI) and the Wheatbelt Drainage Evaluation Project, both commissioned as part of the National Action Plan for Salinity and Water Quality (NAPSWQ).

Figure 1. The Avon River Basin, which contains part of the Western Australian wheatbelt, south west Western Australia

The prospect of increasing volumes of effluent produced by deep drains has increased concerns about the acidic, trace element rich waters that can be produced by such drainage systems and the impacts of these on receiving environments (Dogramaci and Degens 2003). Initial investigations of some major drainage schemes have found that these can discharge waters of pH 2-3 with a salinity of 30000 to 50000 mg/L at 5-10 ML per day (Ali *et al*., 2004b). There are no reports of investigations to characterise the geochemical risks associated with these drainage waters, though limited studies indicate that the waters can contain elevated Al, Mn, Co, Ni and Pb (Ali *et al.,* 2004b; Tapley *et al.,* 2004). Shallow acidic groundwaters likely to be intercepted by the drains can contain significant concentrations of Al, Cu, Fe Mn, Pb and Si (Mann, 1983; Lee and Gilkes, 2005).

A multi-agency research project involving CRC-LEME, CSIRO Land and Water, the Department of Water and the Department of Agriculture was launched in 2004 to quantify the geochemical risks associated with conducting deep drainage at regional scales to control rising saline water-tables in the Avon Basin. The objectives of this study were to:

- Understand the processes of acidic groundwater in the natural or pre-disturbance regolith, and later, beneath the a cleared landscape,
- Forecast the impacts of engineering drainage on the transport and transformation of trace elements in undrained and drained environments, and
- Identify feasible management options (opportunities and constraints) for dealing with the geochemical risks.

This project was initiated to support an EEI funded CSIRO Land and Water project evaluating regional drainage options for the Avon catchment.

Surveys in the Avon Basin have established that acidic drainage waters and shallow groundwaters are widespread in the northern, north-eastern, eastern and south-eastern Avon catchment (Rogers and George, 2005; Fitzpartick *et al.*, 2005) corresponding with the Yilgarn and Lockhart catchments and the northern part of the main Avon catchment (Figure 1). There is in general, a broad range of pH values that can occur in surface waters across the Basin. The pH is usually lowest east of a line from Dalwallinu to Lake Grace (Figure 2) and highest in the western and central WA Wheatbelt (Fitzpatrick *et al.*, 2005).

Acidic groundwaters occur mostly in lower landscape positions, but can also underlie upland landscapes in some areas (Rogers and George, 2005). The cause of this acidity is not certain, though conforms to the hypothesis that iron hydrolysis (ferrolysis) is the dominant cause (Mann, 1983; McArthur *et al.*, 1991). This is where reduced iron in groundwaters is oxidised on exposure to oxygen in air or infiltrating waters, generating H^+ and iron oxyhydroxide precipitates. Broad surveys of groundwaters across the Yilgarn Craton by Mann (1983) indicated that this acidity may predate clearing of the land for agriculture. A simple reaction for ferrolysis can be written as (Mann, 1983):

$$4Fe^{2+} + 6H_2O + O_2 \rightarrow 4FeOOH + 8H^+$$

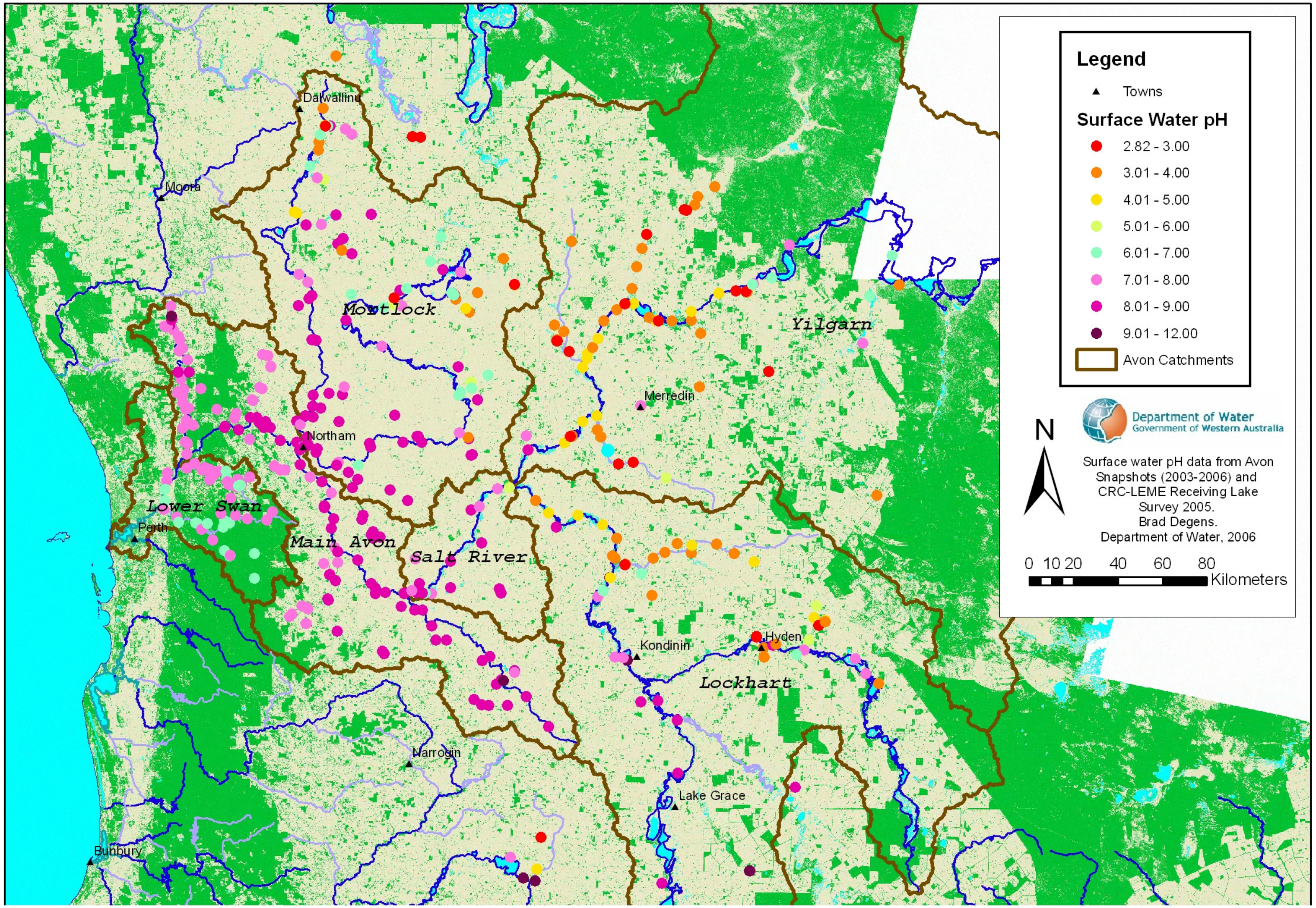
In light of the above, challenges exists to identify methods:

(i) for remediation of the acidic groundwater that are environmentally robust in terms of the safe and efficient immobilization (and if appropriate, disposal) of the contaminants after neutralization,

(ii) for long-term management of the site(s) as required to meet regulatory requirements (*e.g.* van der Sloot, 1996),

(iii) that are easily applied, gain statutory approval and wide community acceptance and are easily integrated into the WA wheatbelt environment, and

(iv) that are cost effective on both a local and regional scale.



Surface water pH data from Avon Snapshots (2003-2006) and CRC-LEME Receiving Lake Survey 2005.
Brad Degens.
Department of Water, 2006

Figure 2. Distribution of pH in surface waters in the WA wheatbelt. Remnant vegetation is shown in green with cleared areas in yellow.

These first three challenges form the basis of this brief review of potential amendments and techniques for the neutralization of acidic waters in the WA wheatbelt. A brief assessment of each amendment or technique is presented, as will a table outlining perceived advantages and disadvantages. Cost is not specifically considered in this review due to the potential for wide cost variation in terms of factors such as transport, infrastructure and running costs for different techniques at specific sites. The amendments and techniques presented in this report are as follows:

- *Carbonates/carbonate derivatives*
- *Mineral processing by-products*
- *Mine overburden*
- *Alkalinity producing systems*
- *Alkaline waters*
- *Landscape modification (burial, re-flooding)*

In this synopsis of potential amendments and techniques we have categorised the remediation of the acidic WA wheatbelt waters as broadly analogous to acid mine drainage (AMD) waters. However, important differences are present. While the primary source of acidity may be different, being predominantly ferrolysis *e.g.* Mann, (1983) and McArthur *et al.,* (1991) with some authigenic pyrite oxidation in drain sediments (Fitzpatrick *et al.*, 2005) for the WA wheatbelt: versus primary sulfide oxidation in AMD, the resultant acidity and high trace element burden presents a similar remediation challenge, that of amelioration of acidity and concurrent trace element reduction. Similarly the mineral suite present within the drainages of the WA Wheatbelt (*e.g.* see Fitzpatrick *et al.*, 2005) and elsewhere is similar to that often observed in AMD (*e.g.* Harris *et al.*, 2003, Ashley *et al.*, 2004) and disturbance of Acid Sulphate Soils (ASS) (Sullivan and Bush, 2004). A key difference, however, is the saline to hypersaline waters often present in the WA wheatbelt relative to the often less saline waters encountered in AMD remediation scenarios.

Although the challenge of remediation of AMD may appear similar in many respects to that that presented in waters of the WA wheatbelt a major contrast is often the prevailing salinity. In general AMD has an ionic strength much lees that that of seawater while many of the WA wheatbelt waters are orders of magnitude more hypersaline. Particular efforts are being undertaken to understand acidification and related processes in saline to hypersaline waters (*e.g.* Fitzpatrick *et al.*, 1998, Bowman *et al.*, 2000, Harris *et al.*, 2003, Bowell and Parshley, 2005, Lee and Gilkes, 2005) and natural attenuation mechanisms such as secondary mineral precipitation (*e.g.* Bigham and Nordstrom, 2000, Lee *et al.*, 2002, Hammarstrom *et al.*, 2005, Buck *et al.,* 2006, Gunsinger *et al.*, 2006). A brief overview of techniques frequently employed to combat AMD, some of which are relevant to the WA Wheatbelt are presented in Gazea *et al.*, 1996, Bowman *et al.*, (2000), Sasowsky *et al.,* (2000), Kuyucak, (2001), PIRAMID 2003a, b, Johnson and Hallberg, (2005), Akcil and Koldas, (2006), Skousen *et al.,* (2006) and references contained therein. Examples of reviews of techniques that may be specifically be applied to acid sulfate soils (ASS), hence ASS forming within wheatbelt drain sediments, can be found in Thomas *et al.*, (2003a) and Thomas, *et al.*, (2003b).

Individual sections below present a background and recent literature associated with particular amendments or acid drainage remediation techniques. In Table 1 a summary of each amendment or technique is presented along with a list of potential advantages and/or disadvantages. These judgments on the particular merits or otherwise of amendment or techniques are general in nature with site specific studies generally required to validate their efficacy. Hence, for this reason, and also due to the large spatial extent of the WA Wheatbelt which may entail substantial transport expenses, no cost estimates have been made.

2 AMENDMENTS AND TECHNIQUES FOR THE NEUTRALIZATION OF ACIDIC DRAINAGE WATERS

2.1 Carbonates/carbonate derivatives

2.1.1 Limestone

The use of limestone to neutralize acidity, whether in constructed wetlands in aerobic or anaerobic settings or added directly to acidic waters/wastewaters is a common practice worldwide (*e.g.* Pearson and McDonnell., 1975a, b, Xu *et al.,* 1997, Sasowsky *et al.,* 2000, Cravotta, 2003, Hammarstrom *et al.*, 2003, Potgeiter-Vermaak *et al.*, 2006, Skousen *et al,* 2006). Hence, limestone amendment may be considered a potential treatment option for similarly acidic waters contained within the WA wheatbelt. Limited studies also suggest that excess limestone may be an effective treatment to prevent sulfide oxidation and consequent acidification (*e.g.* Ward *et al.*, 2002). Limestone dissolution results in the production of calcium and bicarbonate alkalinity. In waters of pH<6.4 limestone reacts as follows (*e.g.* Gazea *et al.,* 1996, Watzlaf *et al.*, 2000):

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3{}^*$$

The dissolved CO_2 denoted as $H_2CO_3{}^*$ is a weak acid that continues to react with the limestone to produce calcium and bicarbonate alkalinity via the reaction:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + HCO_3^-$$

If the pH increases above 9.5 carbonate alkalinity (CO_3^{2-}) may also become significant, however, as caustic alkalinity (OH^-) is converted to bicarbonate alkalinity (HCO_3^-) the pH declines, generally to between 6 and 8. This is generally sufficient to remove trivalent metals (eg Al^{3+}) as hydroxides, but is insufficient to allow the precipitation of many divalent metal ions which may require a higher pH.

While intuitively a simple process for the neutralization of acidity and concomitant precipitation of metals the practical effectiveness of limestone is frequently reduced by precipitated Fe-oxyhydroxides armouring the surface of the limestone, thereby inhibiting its effective reactivity (Sasowsky *et al.,* 2000, Skousen *et al,* 2006). Considerable research has been devoted to overcoming this problem with the most frequent solution being the use of limestone under anaerobic conditions to reduce ferric iron to its ferrous state (*e.g.* Skousen, 1991). Some long-term studies, however, suggest that despite being in an anoxic state, where high (greater than 10's mg/L) aluminium concentrations are present a rapid reduction in permeability leading to wetland failure can occur (Robbins *et al.*, 1996, Watzlaf *et al.*, 2000). The majority of acidic drainage and groundwaters in the WA wheatbelt contain aluminium concentrations in excess of this 10 mg/L threshold.

A summary of the current philosophy on the treatment of acid mine drainage with parallels that can be drawn to waters of the WA wheatbelt are presented in Figure 3 (after Skousen *et al,* 2006). Importantly a recent study on the deposits of limestone available on the South Coast of Western Australia suggest that sufficient limestone deposits are available for in excess of 100 years if the main use is to address soil acidification (Anderson, 1999). Use of these deposits to treat acidic drainage waters would reduce the lifespan of this resource. Additional carbonate resources in inland areas (principally calcrete) are detailed in Anand and Paine (2002). It is likely that a proportion of current limestone/calcrete reserves could be utilized in the treatment of acidic wheatbelt waters, particularly if effective means of combating Fe-armouring are overcome and the carbonate source could be efficiently crushed to create a larger surface area and higher reactivity.

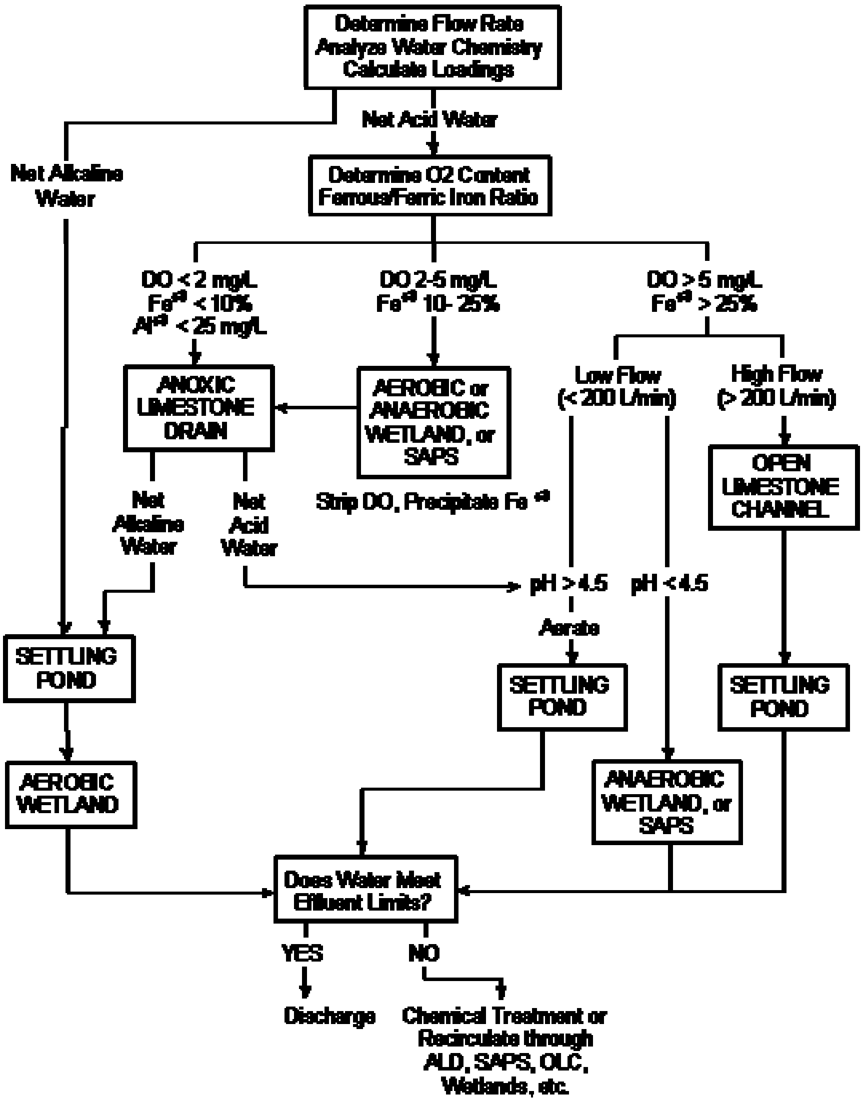


Figure 3. Decision flowchart for selecting a passive AMD treatment system based on water chemistry and flow (Skousen *et al,* 2006 and adapted from Hedin et al., 1994). Acronyms are as follows: ALD – Anoxic Limestone Drain, OLC – Open Limestone Channel, SAPS – Secondary Alkalinity Producing System, DO – Dissolved Oxygen.

2.1.2 Lime[1]

Lime has traditionally been used worldwide as a treatment for AMD (*e.g.* Vachon *et al.*, 1985*,* Kuyucak *et al.,* 1991, Feng *et al.*, 2000, Akcil and Koldas, 2006, Kalin *et al.*, 2006, Skousen *et al.*, 2006). Similarly, lime may also be used in the stabilization of mine tailings with actual acidity and/or acid forming potential (Davis *et al.*, 1999) or in natural soils with potential or actual acidity (Thomas *et al.*, 2003a). The application of quicklime (CaO) results in the rapid formation of $Ca(OH)_2$ in the presence of water as opposed to the often exceedingly slow dissolution (depending primarily on pH) that occurs with limestone (Section 2.1.1) in natural waters:

---

[1] In Western Australia, farmers use commonly use the word "lime" to mean crushed limestone or lime sand. CSBP and DAFWA have programs such as "Time to Lime" etc. Lime as discussed in this section refers to CaO or $Ca(OH)_2$ rather than limestone as $CaCO_3$ which is discussed separately in this review (Section 2.1.1, above).

$$CaO + H_2O \rightarrow Ca(OH)_2$$

and

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

Following dissolution of the hydrated lime, the pH increases and metal ions precipitate as metal hydroxides. Specific metals will precipitate at specific pH values with for instance hydroxides of Fe^{3+}, Al^{3+}, Ni^{2+}, Fe^{2+} and Zn^{2+} beginning to precipitate at pH 3, 3.7-4.5, 8, 8-9 and >9 respectively (Kalin *et al.*, 2006). In addition, because some of the metal hydroxides may be amphoteric in nature, maximum removal efficiency cannot be achieved at a single pH (Feng *et al.*, 2000). Reliably effective precipitation can be achieved in a multi-reagent and multi-stage intensive process (Samvin process, Ramsay, 2001), however, this would be unlikely to be feasible in the context of the treatment of wheatbelt waters. In addition to pH, a number of other factors such as ionic strength, temperature, Eh or redox (all of which may influence mineral saturation states) and precipitated solids may also be influential in trace element removal (Uhlman *et al.,* 2004).

A consequence of applying lime to amend acidity is the production of water abundant in Ca^{2+} and can also result in precipitated gypsum where sulfate concentrations are sufficiently high. The ensuing hardness of waters after lime treatment has the potential to be detrimental to receiving environments (Kalin *et al.*, 2006). In the context of treating saline and hypersaline waters in the WA wheatbelt, however, this factor is probably not important as in most cases gypsum is often at saturation or oversaturation in drains and streams. A further problem with lime can be high residual pH (*ca.* 12) when over application occurs. This can result in a range of deleterious effects including to endemic micro- and macro-biota, with possible re-neutralization of any discharged water required, particularly in sensitive environmental areas. The highly caustic nature of many dry lime products raises the need to implement additional occupational health and safety precautions while transporting and handling these products.

2.1.3 Calcined magnesia

Calcined magnesia (MgO) or its derivative, magnesium hydroxide ($Mg(OH)_2$), possess considerable advantages over other alkalis such as slaked lime ($Ca(OH)_2$) in the neutralization of acids or acidic wastes. The on-going development of a large-scale magnesia industry in Australia will bring distinct advantages in both cost and supply.

One of the most important advantages is the relatively small amount of calcined magnesia (MgO) or magnesium hydroxide ($Mg(OH)_2$) that is required. For the neutralization of 1 tonne of 98% sulphuric acid, only 424 kg of 96% solid MgO, 613 kg of 96% solid $Mg(OH)_2$ or 1005 kg of a 58% slurry of $Mg(OH)_2$ are required. This contrasts with a requirement of 1599 kg of a 50% NaOH solution, 1645 kg of a 45% solution of $Ca(OH)_2$, 3210 kg of a 33% slurry of Na_2CO_3 or 975 kg of $CaCO_3$ (assuming 100% effectiveness).

Additional advantages of calcined magnesia are related to its chemistry (Teringo, 1987, Cortina *et al.*, 2003). Alkalis such as caustic soda or lime can be considered to neutralize by a one-step dissociation reaction that results in the formation of hydroxyl ions and an increase in the solution pH that is often difficult to control. In contrast, the neutralization of acidic solutions by calcined magnesia can be considered to be a two-step reaction as magnesium hydroxide, the intermediate product in the neutralization process is only slightly soluble in water. As a consequence neutralization occurs as soluble hydroxide ions derived from magnesium hydroxide are consumed by the acid. Using sulphuric acid as the acid source, the neutralization reactions can be summarised as follows:

$$MgO + H_2O \rightarrow Mg(OH)_2$$

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$$

$$H_2SO_4 + Mg^{2+} + 2OH^- \rightarrow MgSO_4 + 2H_2O$$

As a consequence of the production of hydroxide ions from the slightly soluble magnesium hydroxide, the neutralization reaction occurs rapidly at low pH and slows appreciably as the pH increases. In addition, varying grainsize can change the reactivity of MgO. In contrast, the neutralization rate of lime and similar products do not vary appreciably as a function of pH. It is the slower reaction rate of calcined magnesia that results in the formation of denser slurries (*e.g.* of mineral precipitates) relative to lime, thus reducing handling and disposal costs. An additional feature of calcined magnesia is the potential for the efficient (and often simultaneous) removal of a range of metals. This removal efficiency is related to the presence of a high pH immediately adjacent to the particle surface. This high pH zone can provide an ideal zone for the precipitation of metal hydroxides which may cement onto the surface of the calcined magnesia substrate.

In the presence of mixed metal solutions which are common in industrial effluents and also within WA wheatbelt drain waters, calcined magnesia also may interact with Fe and/or Al to form a range of mixed layer hydroxide materials generally known as layered double metal hydroxides or sometimes hydrotalcites (Taylor, 1984, Vucelic *et al.*, 1997, Albiston *et al.*, 1996, Shin *et al.*, 1996). A particular property of layered double hydroxides such as hydrotalcites is that a range of metals of widely varying concentrations may also be simultaneously co-precipitated, hence forming a polymetallic hydrotalcite. This has particular relevance to acidic groundwaters (*e.g.* derived from oxidation of acid sulfate soils) and waste streams which may contain a suite of divalent and trivalent metals.

More recent studies on the formation of layered double hydroxides have resulted in the filing of a provisional patent (Douglas, 2006). This new techniques aims to exploit the formation of layered double hydroxides in metal-contaminated acidic plumes using a variety of injection remediation agents including calcined magnesia and magnesium hydroxides as a “virtual curtain” to encapsulate and ameliorate the acidity *in-situ*.

3 MINERAL PROCESSING BY-PRODUCTS

3.1 Steel smelting by-product

Industrial by-products are a ubiquitous legacy of the mineral processing industry. One of the most promising materials to neutralize acidity is steel-making by-product derived from the reduction of iron ore into crude iron. In the United States alone approximately 21 million tonnes of steel industry by-products are produced annually (Proctor *et al.,* 2000). In general, approximately 300kg of by-products is produced for every 1000kg of steel. Locally, the newly commissioned HIsmelt steel-making plant in Kwinana, south of Perth will produce in the order of 200,000 tonnes of steel smelting by-products per annum in full operation.

As part of the steel-making process the by-products are enriched in a range of elements, in particular oxides or more complex minerals containing mostly Mg, Ca and Si. As a consequence these materials, which frequently occur in a fine-grained/glassy and high reactive form, have an inherently high capacity to neutralize acidity, often similar to that of calcium carbonate (*e.g.* Proctor *et al.,* 2000, Simmons *et al.*, 2002, Bayless and Schulz, 2003, Bayless *et al.,* 2004, Ochola and Young, 2004). Although trace element contents may be high in some steel-making by-products, extensive testing suggests that they are not readily leachable (*e.g.* using US EPA TCLP testing protocol, Proctor *et al.*, 2000). In fact some of these by-products have been demonstrated to have a rapid and substantial trace element uptake capacity, particularly when the adsorbate was present as an oxyanion (*e.g.* as PO_4^{3-}, Agyei *et al.*, 2000, or CrO_4^{2-}, Ochola and Young, 2004). An assessment of long-term field disposal sites of steel-making by-products also suggests that these materials have been influential in limiting the mobility of trace elements primarily through the precipitation of secondary minerals such as gypsum (Bayless and Schulz, 2003).

Recent research by CSIRO has devised a method to easily granulate the molten by-product from steel manufacture. The end product resembles small porous marbles which possess a high internal surface area. It is conceivable that this granulated product could be used as channel linings or within wetlands as a reactive substrate to attenuate acidity in WA wheatbelt waters. Wetlands incorporating steel making by-products in combination with limestone pre-treatment wetlands have already been studied as a method to treat AMD (Simmons *et al.*, 2002).

3.2 Red mud/red mud derivatives

Approximately seven million tonnes of red mud is generated per annum in south west WA as a by-product of alumina processing using the Bayer process (Barrow, 1982). Hence, there has been a strong desire, both on the part of aluminium refiners and successive governments to find beneficial uses for this by-product. As a by-product of the Bayer process, red mud is strongly alkaline (pH generally >11), and thus has the potential to ameliorate acidity in AMD effluents or contaminated waters (*e.g.* Doye and Duchesne, 2003, Genc *et al.*, 2003, Winchester, 2005, Lapointe *et al.*, 2006), acid sulfate soils (Lin *et al,* 2002, 2004) or heavy metal contaminated soils (*e.g.* Ciccu *et al.,* 2003). In contrast to the possible application of red mud to ameliorate acidity, numerous studies have demonstrated with varying success that it may also bind phosphorus from effluent or in soils, however, the degree of adsorption may be strongly pH dependant (*e.g.* see Barrow, 1982). Phosphorus adsorption (retention) may also be dependant on the amount of gypsum added to the red mud as an amendment (*e.g.* Jeffery, 1996). It is likely that this high affinity for phosphorus is related to the presence of high concentrations of iron-oxyhydroxides and/or aluminium species in the red mud, although little work has been undertaken to elucidate the exact mechanism of phosphorus retention.

A neutralised red mud produced by a treatment involving seawater has been reported to show some potential in treating acidified soils and drainage waters (*e.g.* McConchie *et al.*, 1996, Ward *et al.,* 2002, Lin *et al.*, 2004, Lapointe, 2006) although studies of red mud neutralization of this type were undertaken almost two decades earlier (Thornber and Hughes, 1987). The seawater neutralization results in a complex mineralogy with a net increase in the acid neutralizing capacity (Lin *et al.*, 2004).

3.2 Fly ash

In excess of 140 million tonnes of fly ash is produced annually as a residue from fossil fuel combustion in coal-fired power stations around the world. At least half of the fly ash is not utilised in a meaningful way, resulting in its disposal as an undesirable landfill which has the potential to cause major environmental problems (Higgins *et al.,* 1976, Theis and De Pinto, 1976, Singer and Berkgaut, 1995). As a consequence of the increasing volume of fly ash generated and its cost of disposal, there is now a desire to utilise fly ash in a productive manner. Given the inherently alkaline properties of many types of fly ash, numerous studies have examined its use to neutralize acid mine drainage in either surface (*e.g.* Scheetz and Earle, 1998, Xenidis *et al*, 2002, Potgieter-Vermaak *et al.*, 2006) or subsurface (*e.g.* Canty and Everett, 2006) environments.

The principal constituents of fly ash are typically silica (*ca.* 30-60% as SiO_2), aluminium (*ca.* 10-30% as Al_2O_3) and lesser amounts of iron and sulfur (Singer and Berkgaut, 1995). Specific types of fly ash, and in particular Class C which is produced from the burning of sub-bituminous coals and lignite have a relatively high calcium content, principally present as CaO, $Ca(OH)_2$ or $CaCO_3$ and thus has substantial neutralization capacity. Trace element abundances are generally high with concentrations of elements such as As, Pb, Cu, Zn, Cd, Cr and Hg typically 1-100 times above average crustal abundances (Theis, 1975). The principal mineralogical constituents of fly ash are impure aluminosilicate glasses (*ca.* 60-90%), with smaller amounts of quartz, mullite, residual coal and ore minerals (Singer and Berkgaut, 1995).

A possible major problem in the application of fly ash in any aquatic system such as acidic wheatbelt drains is the potential for the leaching of high concentrations of trace elements and hence, increasing the load of potentially toxic elements (*e.g.* Hampton, 1974), large increases in pH and high chemical oxygen demand (Theis and De Pinto, 1976). Nonetheless, addition of fly ash to sulfidic wastes has been demonstrated to substantially increase pH to between 8.6 and 10.0 and decrease the dissolved concentrations of contaminants, in particular Zn and Mn (Xenidis *et al.*, 2002). In addition, amendment of acidic soils has been examined in a number of studies (*e.g.* Stehouwer *et al.*, 1994) with up to 1% by weight fly ash increased pH and reduced the leachability of a range of metals (Phung *et al.*, 1979).

4 MINE OVERBURDEN

The Yilgarn Craton underlying the WA wheatbelt is dominated by granite and granitic gneiss rocks with a much lesser amount of basic/ultrabasic rocks (Anand and Paine, 2002). The latter types of rocks may include greenstones and komatiites. The principal mineralogy of these basic to ultrabasic rocks when in their unaltered states generally comprises olivine (*e.g.* forsterite, fayalite), pyroxene (*e.g.* enstatite, diopside) and plagioclase feldspar (albite, anorthite). Many of these minerals, in particular the olivines and pyroxenes have an inherently high capacity to neutralize acidity over the long-term (Figure 4). In addition, alteration minerals that may form during the weathering process and are known to be present in the Yilgarn regolith include a range of carbonates present within the lower weathering profile which may only be uncovered during mining activities.

Mine overburden has an intrinsically low value and thus if near to sources of acidity could conceivably be used as a long-term neutralizing agent. Factors that may count against its use include the necessary processing of the overburden to increase its effective surface area and reactivity (*i.e.* crushing) and the filling of drains or receiving environments. In addition, surface area may not only limit to neutralising capacity with the alkalinity in practice only available at the effective rate of mineral weathering.

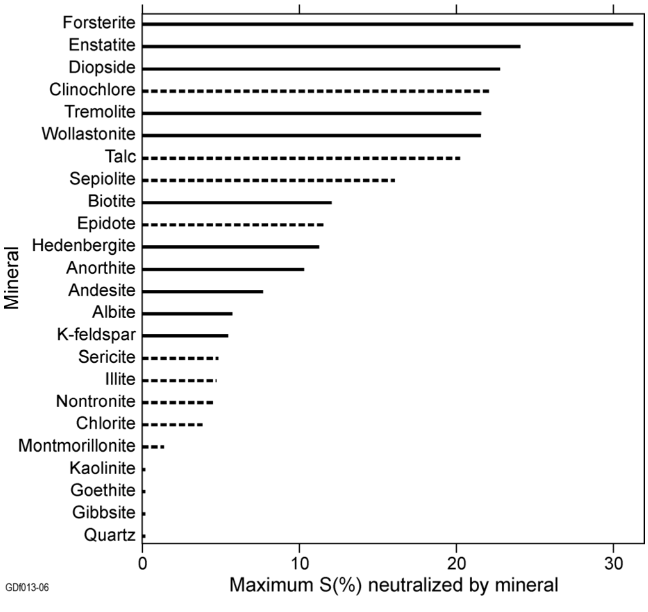


Figure 4. Buffer capacity in near neutral solution of a range of common minerals (solid lines) and their alteration products (dashed lines). The estimated buffer capacity is the maximum percentage of S that can be neutralized by the mineral (modified after Risacher *et al.*, 2002). This assumes an infinite amount of time for reactions or containment of net-acidic materials with net-alkaline minerals.

5 ALKALINITY PRODUCING SYSTEMS

Bacterial sulfate reduction is a technique frequently employed in both artificial wetlands for the treatment of AMD (*e.g.* Evangelou and Zhang, 1995, Kalin *et al.*, 2006, Skousen *et al.*, 2006) and bioreactors (*e.g.* Kaksonen *et al.*, 2003, Kaksonen, 2004) for the neutralization of acidic waters and concurrent removal of trace metals. A summary of the process involving the microbial oxidation of organic matter and reduction of sulfate that results in the release of HCO_3^- and HS^- as by-products according to the reactions is given in Gazea *et al.*, (1996) and Johnson and Hallberg (2005) and summarized below:

$$\text{Bicarbonate: } 2CH_2O + SO_4^{2-} \rightarrow HS^- + 2HCO_3^- + H^+$$

$$\text{Hydrogen sulfide: } 2CH_2O + SO_4^{2-} + 2H^+ \rightarrow H_2S + 2H_2O + 2CO_2$$

Where CH_2O represents organic matter or a high energy carbon source (*e.g.* ethanol).

Metal precipitation is initiated by the increase in pH (due to bicarbonate alkalinity) and the presence of hydrogen sulfide according to the reaction:

$$M^{2+} + H_2S \rightarrow MS + 2H^+$$

Where iron is present pyrite may form according to the reaction:

$$Fe^{2+} + H_2S + S^0 \rightarrow FeS_2 + 2H^+$$

Pyrite formation may also result in co-precipitation (as sulphides) of a range of trace elements from treatment waters.

In the context of the WA wheatbelt, a bioreactor could involve a high sulphate reducing system, using ethanol dosed feed-waters or a slower sulphate reducing system driven by organic matter. Recent work at CSIRO has demonstrated that high rates of acid water treatment and metal removal can be achieved using an ethanol-fed bioreactor (Kaksonen *et al.*, 2006), although to achieve similar treatment efficiencies using acidic saline waters required much greater residence times (*pers.comm.* Peter Franzmann, 2006). The high maintenance requirements of such a reactor may limit application to pre-treatment of acidic ground-waters to increase pH and reduce the dissolved metal load prior to desalination for the production of a potable water resource. Specific advantages of a bioreactor are as follows:

- Highly effective neutralisation of pH from pH as low as 2 to 3.
- Separation of liquid and solid phases means effective removal of all precipitated metals and salts from water
- Capture of sulfide products removes source of future acid generating material
- Metal sulfides and salts may have commercial value
- Minimal production of sludge for disposal as might be the case for application of lime

Potential disadvantages in the use of a bioreactor are as follows:

- Process has an ongoing maintenance/operational requirement
- An energy source for growth of sulfate reducing bacteria is required for the process (usually ethanol to achieve high rates of sulfate reduction)
- Some production of mal-odourous H_2S may occur
- There is an on-going power requirement for pumps

- The bioreactor process may not operate optimally for all highly saline waters (> seawater salinity), which are frequently present in the large regions of the WA wheatbelt

More passive bioreactor systems can also achieve treatment of acidic, metal laden water using constructed wetlands (often called compost wetlands or anaerobic wetlands; *e.g.* Skousen *et al.*, 2006 and PIRAMID, 2003a, b). This involves the use of straw or other available organic matter sources (eg wood chips, green waste or paper pulp) to encourage formation of anaerobic conditions and initiation of sulphate reduction. Sulfate reduction is commonly a slow process in such wetlands (*e.g.* Machemer *et al.*, 1993) and often requires large areas to allow enough residence time for waters (*ca.* days-weeks) for effective reduction of metal concentrations to take place. The low maintenance (and long-life) aspects of the treatment systems may make these suitable for on-going treatment of acidic drainage waters with low, continuous acid loads (<50 tonnes equivalent $CaCO_3$/annum).

6 ALKALINE WATERS

Alkaline surface waters in natural and artificial drainages are present at a number of locations in the WA wheatbelt (Figure 2) that may offer some possibilities for neutralising and treating acidic drainage waters. Regolith type and elevation are likely to be major determinants of the presence and quantity of alkaline waters, however, with the majority of acidic bores as a source for acidic drains occurring in alluvium and the seasonality of flow with major flows generally considerably more alkaline. In addition, drain waters generally have a bimodal pH distribution between either 3.0-4.5 or 6.0-8.5. This variation in pH probably reflects both source and current/antecedent flow conditions. Furthermore, oxidation of sulfidic minerals within valley floors (Fitzpatrick *et al.*, 2005) or drains, particularly at low flows where ponding, desiccation and oxidation of sulfides to sulphuric acid occurs may also represent an additional *in-situ* acidity (and trace element) source.

As outlined in the introduction, a broad range of pH values can occur in surface waters across the wheatbelt. The pH of surface waters is usually lowest east of a line from Dalwallinu to Lake Grace (Figure 2) and highest in the western and central WA Wheatbelt. Thus, it would seem that pumping and/or construction of conveyance drains would need to occur to achieve mixing of acidic with alkaline waters. In addition, it may be difficult to justify use of frequently limited alkaline surface waters to neutralize acid waters (in terms of net environmental gain) in a landscape where non-acidic waters would be essential for the maintenance of remnant ecosystems. Additional sources of alkaline waters may be yielded during flood events particularly from the upper Yilgarn and Lockhart catchments. However, these would not occur on an annual basis and spatial occurrence of these would need to be considered in relation to containment of acidic waters.

The use of alkaline waters in acidic drainages would require careful basin-wide management of acidic waters and neutralisation products. In particular, the flushing of formerly dry or ponded drains or receiving basins by acidic to neutral pH waters, in particular those with insufficient alkalinity to ameliorate the immediate acidity burden, may result in three processes:

(i) dissolution of sulfate and other mineral efflorescences formed during the drying phase leading to remobilization of trace elements (*e.g.* Harris *et al.*, 2003, Fitzpatrick *et al.,* 2005),
(ii) mobilization of acidity and concomitant trace elements within disconnected ponds or within shallow porewaters, and
(iii) where insufficient alkalinity is available for complete neutralization, the transfer of acidity and trace elements to sensitive receiving environment downstream.

7 LANDSCAPE MODIFICATION (BURIAL, RE-FLOODING)

A potential management option to ameliorate acidity within deep drains of the WA wheatbelt is the use of both local- and broader-scale landscape modification to achieve changes in drain and/or subsurface Eh-pH conditions. Such options include selective in-fill of drains with encapsulation of acidic sediments and re-flooding of drained profiles.

Where artificial drainages can be identified which have little intrinsic value in terms of their drainage capacity, re-burial or in-fill is an option to encapsulate acidity accumulated within drain sediments. This may involve the in-filling of deep drains that intercept acidic groundwater and replacement with shallow drains that only remove excess surface flow where appropriate. The burial of drains that could remove or reduce the oxygen supply and slow or eliminate the rate of sulfide oxidation (*e.g.* from authigenic sulfide minerals formed within the drainage channels) and reduce the rapid discharge of acidic ground-waters. This strategy has been considered in disturbed coastal acid sulfate soil environments (Bowman *et al.*, 2000, Fitzpatrick *et al.*, 2003) and may be adapted to some wheatbelt drains to manage acidic waters.

Studies on partially oxidised acid sulfate soils also suggest that anoxia that may typically be generated by burial of acidic sediments may lead to sulfide re-formation, particularly where organic matter was available (Ward *et al.*, 2004). Nonetheless, acid generation via ferrolysis within the unique setting of the WA wheatbelt (Mann, 1983, McArthur *et al.*, 1991) coupled with often high water tables remains a consistent source of acidity.

In many cases avoiding further disturbance by deep drainage of the shallow regolith may not circumvent discharge of acidic waters to surface landscapes over the long-term, particularly near sensitive remnant receiving environments of high ecological value. A further consideration is that any possible in-fill of drains has to be compatible with local and more regional attempts to instigate deep drainage as a solution for salinity and acidity management.

A second possible management option to ameliorate acidity within deep drains in the WA wheatbelt is the selective re-flooding, perhaps in combination with drain-in-fill as described above. Previous attempts at re-flooding have principally focussed on coastal acid sulfate soils using seawater with its inherent acid neutralization capacity due to the presence of bicarbonate and the extensive flushing and dilution often present in coastal areas. Limited studies have also examined the use of freshwater flooding (*e.g.* Thomas *et al.*, 2003a, b). Importantly, however, even in the event of flooding, partial oxidation of pyrite in drain sediments by Fe^{III} may still occur (Bowman *et al.*, 2000). Nonetheless it has been identified by Thomas *et al.*, (2003a, b) that some benefits of watertable control via flooding are:

- less additional acid may be generated;
- the frequency of acid release is reduced;
- the concentration of acid released is minimised;
- the volume of acid groundwater released is reduced;
- vegetation and organic matter cover is increased;
- habitat values are improved including vegetation survival following inundation; and
- problems with low dissolved oxygen are minimised.

Given the limited supply of water with sufficient alkalinity (see Section 6) it is likely that only small areas of the landscape may be amenable to re-flooding. Suitable trial areas would be highly ecologically sensitive areas where there is a local source of alkaline water and area for sufficient infrastructure to be put in place that would allow complete mixing and attenuation of acidity. Application of this approach would need to consider the impacts on hydrology in comparison with the impacts of acid drainage, since re-flooding would be incompatible with the objective of using deep drainage to reduce local and regional saline ground-water levels to ameliorate dryland salinity.

Table 1. Summary of remediation options for treatment of acidic saline drainage waters in the WA wheatbelt.

Amendment/technique	**Description**	**Advantages**	**Disadvantages**	**Potential suitability**
Carbonates/derivatives				
Limestone/calcrete/ limesand	Limestone, limesand and calcrete are common throughout coastal and inland WA respectively. Could also include dolomite	Cheap, abundant, generally pure source.	May require crushing. Fe-armouring during use. In constructed wetlands high Al may present problems (see text). Incorporation into drain sediments and net loss.	Potential applications in constructed wetland, drain lining or soil barriers. Transport costs may present a barrier for widespread use, processing and application costs. Possible surface application to acid pond/scalds. Could be combined with an active dosing unit to increase effectiveness.
Lime	Quicklime: CaO or slaked lime: $Ca(OH)_2$.	Cheap, abundant, pure, commercially available.	Difficulty in controlling dosing may result in high pH waters. Increased water hardness. Low density flocs (prone to down-stream transport). Transport, greenhouse (CO_2) emission.	As for limestone/calcrete.
Calcined magnesia or magnesium hydroxide	Calcined magnesia: MgO or: $Mg(OH)_2$.	Low sludge, better pH control. Safer handling, less needed than lime.	Transport cost, greenhouse (CO_2) emission. Higher density flocs vs lime. Water hardness.	As for limestone/calcrete.
Mineral processing waste				
Red Mud and derivatives	Red Mud, Bauxsol.	High alkalinity, with seawater amendment possible.	Transport from coastal. A “waste”, - previously poor acceptance for use in waterways.	As for limestone/calcrete.
Fly ash	By-product of lignite/coal combustion.	Cheap, coal-fired power stations, highly alkaline.	High trace element content, transport., long term stability, possible oxyanion.	As for limestone/calcrete. Trace element content may negate benefits.
Sourced from Fe-ore smelting.	Glassy Ca- and Mg-silicate material.	By-product is cheap, clean. Acid neutralizing capacity similar to limestone.	Transport from a coastal region, crushing, although pelletization is possible.	As for limestone/calcrete.
Mine overburden				
Regolith materials	Soils/regolith with high acid neutralizing capacity.	Potentially cheap, industry assistance in disposal, close proximity to eastern wheatbelt (some sites)	Contaminants may be present in regolith materials. Crushing and processing costs, Rate of and total acid-neutralization capacity varies widely.	As for limestone/calcrete.

Table 1. (contd). Summary of remediation options for treatment of acidic saline drainage waters in the WA wheatbelt.

Amendment/technique	**Description**	**Advantages**	**Disadvantages**	**Potential suitability**
Alkalinity producing systems				
Bioreactor	Intensive ethanol-fed biological treatment process to recover metal sulfides.	Self-contained, high sulfide removal efficiency, low sludge, operates from pH2 upwards.	Cost, infrastructure, disposal of sulfidic solids. Energy source (ethanol). Mal-odourous (H_2S). Less effective with high salinity waters.	Pre-treatment (neutralization and metal removal) from acid saline water prior to desalination.
Compost/Vegetated wetland treatment	Compost/plant driven biological treatment systems (generating alkalinity and trap trace metals.	Self-contained, compost or plant-based wetland system, long-term low input treatment (use existing on-farm organics *e.g*. straw).	Construction cost, large areas needed, slow treatment rates, infrastructure, long-term containment of sulfidic solids.	Low acid discharge treatment systems (end of drains) or in-drain treatment for low flow or low acidity drains.
Alkaline waters				
Naturally occurring alkaline waters	Use of alkaline flood or winter surface waters, in central or far eastern wheatbelt.	Cheap source, utilizes existing resources in wheatbelt, may be applicable at broader scales (pending further investigation).	Loss/redirection from sensitive ecosystems. Seasonality and inter-annual variation in alkaline water flows, limited spatial extent. Uncertain minimum scale of application.	Reasonable potential, though disconnection of acidic and alkaline waters (floods) by time and space may be a problem. Develop model to estimate amounts/water quality and timing of mixing/neutralisation.
Landscape modification				
Instigate local or regional changes in hydrology, drainage or relief	Re-burial and/or re-flooding of drains or wider landscape	Low-maintenance, long-term treatment of acidic sediments and containment of acidic waters.	Outcome uncertain in particular regions. May conflict with objective of reducing saline ground-water levels. Significant on-ground information needed to commence.	Good potential in specific areas where local hydrology and geo-chemistry is well understood.

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