Selection of active and passive treatment systems for AMD—flow charts for New Zealand conditions

D Trumm*

CRL Energy Limited, Christchurch, New Zealand

(Received 22 September 2009; final version received 6 October 2010)

Treatment of acid mine drainage can be accomplished by either active or passive treatment systems. Choice between active and passive treatment and appropriate selection of systems within each category is critical for treatment success. In general, active treatment is more commonly used at operational mines whereas passive treatment is typically considered for closed and abandoned mines. Operational mines often have limited space for remediation systems and have large and fluctuating flow rates with changing drainage chemistry as mining proceeds, factors that are addressed more easily with active than passive treatment. In the long term, passive treatment could offer more economic options than active treatment. Various flow charts have been prepared by previous researchers to help select among the passive systems but little work has been done to help select between active and passive treatment or to select appropriate active treatment systems. Furthermore, the passive treatment flow charts have often not included variables important for application to New Zealand sites: topography, climate and available land area. Very steep topography, dense and often protected vegetation, and a high-rainfall climate may result in acid mine drainage with high flow rates in locations with limited space for remediation. This paper presents flow charts specific to New Zealand which have been prepared to accommodate topography and available land area.

Keywords: acid mine drainage; iron; aluminium; manganese; remediation; treatment

Introduction

Acid mine drainage (AMD) is a common issue associated with coal mining in New Zealand. It has been documented at both active and abandoned mines, both opencast and underground in various areas but mostly on the West Coast (Alarcon 1997; deJoux 2003; James 2003; Black et al. 2005; Pope et al. 2006). The severe effects of AMD on the aquatic ecosystem have been extensively studied (Winterbourn 1998; Harding & Boothryd 2004; Harding 2005).

Treatment can be accomplished by either active or passive techniques (Skousen et al. 2000; Waters et al. 2003). Choice between active and passive treatment and appropriate selection of systems within each category, however, is critical for treatment success. Various flow charts have been prepared by previous researchers to help select which type of passive system is suitable but little work has been done to help select between active and passive treatment, or to select appropriate active treatment systems. The work here presents flow charts specific for New Zealand conditions to select between active and passive treatment and to select specific treatment systems within each category based on site-specific parameters.

Selection between active and passive treatment

Active treatment systems typically require equipment (e.g., tanks, mixers, pumps), regular operation and maintenance, continuous dosing with chemicals, and power but they are more reliable than passive systems (Younger et al. 2002). Their main advantages include: effective removal of contaminants from mine drainage (e.g., acidity and metals), precise process control such that they can be engineered and operated to produce a specific water chemistry, and suitability in locations where only a small land area is available. (Although very high flow rates may require substantial land area for sludge capture unless clarifiers and thickeners are used.) The main disadvantages of active treatment are the high capital cost and high ongoing operation and maintenance costs. Active treatment is more suited to operational mine sites, which typically have limited land area available for remediation systems, changing drainage chemistry and flow rate, and have power and personnel to manage the treatment system.

Power is a critical factor for active treatment systems. Pumps are often used to convey the water to the plant and between various components of the system, power is usually needed to meter additives to the water such as neutralising chemicals, flocculants, and coagulants, and power is necessary for mixing and oxidation of the water. If no power is available at the site, a semi-passive system, such as the Aquafix system, can be used which relies on a paddlewheel in the AMD stream to operate a hopper that dispenses neutralising chemicals into the AMD (Skousen & Jenkins 1993). Otherwise, lack of power limits AMD treatment to passive systems unless it is warranted to bring power to the site.

*Corresponding author. Email: d.trumm@crl.co.nz
Passive systems rely on natural physical, geochemical and biological processes but can fail if not carefully selected and designed (Skousen et al. 2000). Unlike active treatment systems, which add neutralising material on a regular basis to neutralise the acidity in AMD indefinitely, passive systems are usually constructed with a lifespan (25 yr) of neutralising material such that no additional inputs are necessary. Most passive treatment systems rely on the dissolution of a neutralising material (usually limestone) to neutralise the acidity in AMD and sufficient residence time in the systems is necessary for this dissolution to occur. As such, passive systems typically require large areas of land and are more suited to complement active systems or closed mine sites. However, in the long term, treatment using passive systems is often more economical than active systems especially after mine closure (Skousen et al. 2000; Skousen & Ziemkiewicz 2005). AMD at closed and abandoned mines often has a more stable chemistry and flow rate than at active mines and land is usually more readily available for remediation systems, factors that fit well with passive treatment.

Characteristics of the seven most commonly used chemicals in active treatment such as maximum pH attainable, neutralisation efficiency, cost, dispensing mechanism, benefits, and limitations are included in Table 1. Characteristics of the ten most common passive treatment systems such as general descriptions, design factors, cost, benefits, and limitations are included in Table 2.

There are a number of factors that will influence the decision as to whether to use active or passive treatment (Fig. 1). Briefly, if a mine drainage exceeds specific thresholds, large amounts of neutralising material is required to ensure appropriate treatment. In this case a large passive system would be required, which can be prone to failure, and active treatment is likely to be a better choice. Variables particularly relevant in New Zealand include flow rate and acid load. The West Coast region, where the majority of AMD sites are located, has a relatively high annual rainfall (up to 6 m on the plateaus north of Westport), and AMD sites are often located in very isolated areas with steep topography. This can result in AMD with very high flow rates and acid loads which can be markedly influenced by rainfall events. This is very different to the southeastern USA (West Virginia) where much of the early development of AMD treatment occurred. There, topography plays a minor role in the selection of treatment systems and the dominant climatic variables are the very cold winters and hot summers. As such, base and peak flow rates and acid loads for New Zealand AMD sites need to be carefully considered along with the degree of isolation and access to power when making a choice between active and passive treatment. Further details of how each parameter influences the choice of active or passive treatment are provided below.

### Acidity and pH

Acidity is comprised of proton acidity (pH) and mineral acidity, which is from dissolved metal species that produce more proton acidity upon hydrolysis (Rose & Cravotta 1998). To treat a low pH and/or high acidity AMD with passive remediation, a very large system is necessary to achieve a long enough residence time for neutralisation and a very large amount of neutralising material is necessary to maintain system longevity. Very large systems can be prone to short circuiting and failure as preferential pathways may develop over time. Rather than constructing one large system, it would be better to split the flow among several parallel systems. Waters et al. (2003) document that most successful passive treatment systems treat AMD with pH greater than 2 and acidity less than 800 mg/L (as CaCO₃). The relationship between acidity and pH is exponential, with much greater increases in acidity below pH 2 (Fig. 2). An acidity of 800 mg/L equates to a pH of 2 with an Fe concentration of 50 mg/L and Al concentration of 30 mg/L. As such, AMD with extremely low pH (<2) and/or high acidity (>800 mg/L) is better treated with active systems than passive systems.

### Flow rate

High flow rates are difficult to treat with passive systems because the systems need to be very large to achieve the necessary residence time and very large systems can be prone to short circuiting and failure. However, flow rates should be carefully considered along with the practicalities of treatment. Significant flow rate variations during storm events are common at AMD sites in New Zealand, and treatment systems (active or passive) may not be able to treat the AMD 100% of the time, but rather might be designed for base flow conditions and allow high flow events to bypass the treatment system. Before this decision can be made, quantification of acid loads during base flow versus total flow (including storm events) should be completed and compared to the treatment requirements for the site. In general, active treatment systems can accommodate some variability in flow rates by changing chemical dosing rates to match flow rates, whereas passive treatment systems can only manage variability if an equalisation header pond is constructed to dampen peak flows.

### Acid load (acidity x flow rate)

A high acid load (generated by high acidity and/or high flow) consumes the neutralising material faster, and in a passive system this can limit life expectancy. In addition, high flow rates require construction of very large systems that can be prone to short circuiting and failure. Therefore, for a situation with very high acid load, it is recommended to consider using an active treatment system, although a passive system can perhaps be used if a shorter life...
Table 1 Table of characteristics of chemicals used to neutralise AMD in active treatment systems (compiled from Skousen et al. 2000; Waters et al. 2003; Means 2006)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Max pH attainable</th>
<th>Conversion factor</th>
<th>Neutralisation efficiency (%)</th>
<th>Cost of chemical</th>
<th>Dispensing mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda ash or sodium carbonate (Na₂CO₃)</td>
<td>11.6</td>
<td>1.06</td>
<td>95–100 (powder) 60 (briquettes)</td>
<td>$830–$870</td>
<td>Briquettes or powder placed in wooden box or large drum/reactor in AMD stream.</td>
</tr>
<tr>
<td>Hydrated lime or calcium hydroxide (Ca(OH)₂)</td>
<td>12.4–12.5 0.74</td>
<td></td>
<td>90–95</td>
<td>$330–$350</td>
<td>Silo or hopper with mechanical feed screw to dispense powder.</td>
</tr>
<tr>
<td>Quicklime or calcium oxide (CaO)</td>
<td>12.4–12.5 0.56</td>
<td></td>
<td>90–95</td>
<td>$221–$233</td>
<td>Silo or hopper with mechanical feed screw to dispense powder or water wheel feeder</td>
</tr>
<tr>
<td>Ammonia (NH₃ or NH₄OH)</td>
<td>9.2</td>
<td>0.34</td>
<td>100</td>
<td>$2200</td>
<td>Compressed and stored as liquid in tank, gas injected near bottom of pond or water</td>
</tr>
<tr>
<td>Caustic soda or sodium hydroxide (NaOH)</td>
<td>14</td>
<td>1063</td>
<td>100</td>
<td>$1050</td>
<td>Stored as a liquid in tank, dispense through metering pump or valve</td>
</tr>
<tr>
<td>Magnesium oxide or hydroxide (MgO or Mg(OH)₂)</td>
<td>9–9.5 0.40 or 0.58</td>
<td>Not common in NZ</td>
<td>90–95</td>
<td>$111</td>
<td>Silo or hopper with mechanical feed screw to dispense powder.</td>
</tr>
<tr>
<td>Limestone (CaCO₃)</td>
<td>6–7.5</td>
<td>1</td>
<td>approx. 90</td>
<td></td>
<td>Silo or hopper with mechanical feed screw to dispense powder.</td>
</tr>
</tbody>
</table>

1 Conversion factor is the mass of chemical needed to neutralise the acidity relative to limestone. The conversion factor is used along with the neutralisation efficiency to calculate the tonnes of chemical needed to neutralise each tonne of acidity per year. For sodium hydroxide, the conversion factor gives litres of chemical needed per tonne of acid.

2 Neutralisation efficiency estimates the effectiveness of the chemical in neutralising acidity relative to sodium hydroxide and is used along with the conversion factor to calculate the tonnes of chemical needed to neutralise each tonne of acidity per year. For example, if 46 tonnes of acid needs neutralisation per year, 38 tonnes of hydrated lime would be needed [46(0.74)/0.90].

3 Cost of chemical is per tonne of acid neutralised in 2010 New Zealand dollars. This is an effective way to compare costs of treatment with different chemicals. Cost is calculated using purchase price, conversion factor and neutralisation efficiency. For example, if calcium oxide costs $375 per tonne, to neutralise 1 tonne of acidity would cost $233 [(375)(0.56)/0.90].
<table>
<thead>
<tr>
<th>System type</th>
<th>General description</th>
<th>Design factors</th>
<th>Key benefits</th>
<th>Limitations</th>
<th>Construction cost</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidising strategies</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Open Limestone Channels (OLC)</strong></td>
<td>Channel, ditch, or streambed lined with limestone cobbles. Dissolution of limestone and neutralisation occurs as AMD flows down the channel.</td>
<td>Rock sizes should be &gt; 10 cm (15–30 cm). Slope should be &gt; 20%, if possible. Base residence time on acid load, limestone volume on alkalinity generation rate.</td>
<td>Low cost, Simple. High level of reliability.</td>
<td>Armouring with hydroxides. Can construct at &gt;20% gradient to minimise but then must be long channel to achieve residence time.</td>
<td>$134,758</td>
<td>Ziemkiewicz et al. 1994; 1997; Ziemkiewicz &amp; Brant 1996; Cravotta &amp; Trahan 1999; Trumm et al. 2005, 2008</td>
</tr>
<tr>
<td><strong>Open Limestone Drains (OLD)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Diversion Wells (DW)</strong></td>
<td>Round chamber filled with crushed limestone aggregate. AMD flows into chamber out pipe near bottom of well creating turbulence which abrades particles preventing armouring. Water flows upward and out of chamber.</td>
<td>Design based on trial and error. Well dimensions typically 1.5 m diameter, 2 m deep, 1/2 filled with 1–2 cm diameter limestone gravel (low hardness). Residence time about 15 min.</td>
<td>Low cost. High limestone efficiency.</td>
<td>Requires refilling with limestone chips about every 2–4 weeks. Requires elevation change and constant flow rate. Precipitates not captured. Pockets of air in piping can reduce flow rate.</td>
<td>NA</td>
<td>Sverdrup 1983; Arnold 1991; Faulkner &amp; Skousen 1995; Skousen et al. 1998</td>
</tr>
<tr>
<td><strong>Limestone Leaching Beds (LLB)</strong></td>
<td>Rectangular chamber filled with limestone cobbles. AMD flows horizontally or vertically through cobbles dissolving limestone which neutralises acidity.</td>
<td>Limestone mostly between 38 and 90 mm size. 15 h residence time in leaching bed.</td>
<td>Simple. High level of reliability.</td>
<td>Armouring with hydroxides if Fe concentrations too high.</td>
<td>$151,061</td>
<td>Black et al. 1999; Danehy et al. 2002; Hilton et al. 2003; Watzlaf et al. 2004</td>
</tr>
<tr>
<td><strong>Slag Leaching Beds (SLB)</strong></td>
<td>Rectangular chamber filled with steel slag fines. AMD flows horizontally or vertically through slag dissolving CaO which neutralises acidity.</td>
<td>Steel slag mostly less than 3 mm. Residence time 1–10 h depending on acidity.</td>
<td>High pH. Generates more alkalinity than limestone (up to 2000 mg/L). Stable silicate sludge produced.</td>
<td>Armouring with hydroxides. Slow dissolution. Leaching of metals from slag.</td>
<td>NA</td>
<td>Ziemkiewicz &amp; Skousen 1998; Simmons et al. 2002; Trumm et al. 2009</td>
</tr>
<tr>
<td><strong>Aerobic Wetland</strong></td>
<td>Large surface area pond with emergent wetland species plants. With or without limestone. AMD flows horizontally through pond and over substrate. Oxidation reactions precipitate oxides and hydroxides.</td>
<td>Design based on removal rates: 10–20 g Fe/m²/d, 0.5–1 g Mn/m²/d, 3.33 g H₂SO₄/m²/d.</td>
<td>General precipitate storage. Low cost.</td>
<td>Best for pH &gt; 5.5. Removes selected metals.</td>
<td>$25,349</td>
<td>Skousen et al. 1992; Hedin et al. 1994; MEND 1999; Tarutis et al. 1999; Skousen et al. 2000; Batty and Younger 2002</td>
</tr>
<tr>
<td><strong>Dosing with Limestone Sand</strong></td>
<td>Large stockpile of crushed limestone placed on edge of AMD. Water washes limestone into stream and acidity neutralised.</td>
<td>Limestone very small grain size. Stockpile placed partly in stream.</td>
<td>Very simple, armouring prevented due to small grain size.</td>
<td>Requires restocking pile.</td>
<td>NA</td>
<td>Mills 1996; Zurbuch 1996; Skousen et al. 1998; Watzlaf et al. 2004</td>
</tr>
</tbody>
</table>
expectancy (<25 years) is acceptable. This will often be based on a cost benefit assessment of active versus passive treatment. Alternatively, if sufficient space is available at the site, the AMD can be split into several smaller flows with lower acid loads and multiple passive treatment systems can be constructed. This is essentially using a process principle to enable use of passive treatment in a high acid load situation. High acid loads can also result in much greater volumes of precipitates generated during neutralisation and the longevity of passive systems can be

Table 2 (Continued)

<table>
<thead>
<tr>
<th>System type</th>
<th>General description</th>
<th>Design factors</th>
<th>Key benefits</th>
<th>Limitations</th>
<th>Construction cost¹</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducing strategies</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anaerobic Wetlands</td>
<td>Large pond with a layer of organic substrate, typically spent mushroom compost with about 10% CaCO₃. AMD flows horizontally within the substrate. Emergent vegetation helps stabilise substrate and provide organic material. Sulphate reduction removes sulphate and metals.</td>
<td>Hydraulic conductivity of substrate 10⁻³–10⁶ cm/s. Design based on removal rates: 3.5 g acidity/m²/d; 2.9 g H₂SO₄/m²/d; sulphate reduction rate 300 mmoles/m³/d.</td>
<td>Relatively stable sulphide sludge storage.</td>
<td>Requires long residence time.</td>
<td>$57,938</td>
<td>Hedin et al. 1994; Skousen et al. 1992; Skousen et al. 2000</td>
</tr>
<tr>
<td>Vertical Flow Wetlands (VFW); Successive Alkalinity Producing System (SAPS); Reducing and Alkalinity Producing System (RAPS)</td>
<td>A rectangular unit with limestone at the base covered by spent mushroom compost and free water. AMD flows vertically down through the unit. Sulphate reduction removes sulphate and metals in the compost, alkalinity generated in limestone.</td>
<td>15–30 cm organic matter; 6–15 cm diameter limestone. Design based on 15 h residence time in limestone layer; 35–40 g acidity/m²/d removal rate.</td>
<td>Small area required. Good for high Fe, low Al.</td>
<td>High capital costs. Armouring and plugging with hydroxides.</td>
<td>$171,250</td>
<td>Kepler &amp; McCleary 1994; Nairn &amp; Mercer 2000; Watzlaf et al. 2000; Zipper &amp; Jage 2001; Thomas &amp; Romanek 2002; Watzlaf et al. 2004; Rose 2006</td>
</tr>
<tr>
<td>Sulphate Reducing Bioreactor (SRB)</td>
<td>A rectangular unit filled with a mixture of organic substrates such as hay, alfalfa, sawdust, paper, or woodchips, crushed limestone, and compost or manure. AMD flows vertically through unit. Sulphate reduction removes sulphate and metals.</td>
<td>Design based on removal rates: −0.3 mol metals/m² of substrate/d or 0.3 mol sulphate/m²/d.</td>
<td>Small area required. Good for high Fe, low Al.</td>
<td>High capital costs. Reduced permeability with time. Potential for armouring and plugging with hydroxides.</td>
<td>$273,876</td>
<td>Gusek 2002; Gusek 2004; Neculita et al. 2007</td>
</tr>
</tbody>
</table>

¹ Cost to treat hypothetical AMD shown in 2010 New Zealand dollars (Acidity 150 mg/L, Fe²⁺ 10 mg/L, Fe³⁺ 1 mg/L, Al 12 mg/L, pH 2.9, DO 1 mg/L, flow rate 10 L/s) determined using AMDTreat (US Office of Surface Mining Reclamation and Enforcement, Pittsburgh, Pennsylvania, USA) computer program.
compromised if permeability drops as precipitates accumulate in system pore spaces (Waters et al. 2003).

As discussed above, significant flow rate fluctuations are common at AMD sites in New Zealand, and systems (active or passive) must be designed with this in mind. Research is lacking on the effect of flow rate fluctuations on acid load in New Zealand; it is possible that correlations may be site-specific and even variable for a given site. Research is also lacking on the effect on the ecosystem from a sudden pulse of high acid load water if treatment systems are not designed to accommodate storm events where acid loads are increased. It is recommended that these issues be addressed prior to deciding level of treatment required.

**Active treatment**

Active treatment for AMD is largely based on industrial wastewater treatment technologies (United States Environmental Protection Agency [USEPA] 1983; Younger et al. 2002). There are a variety of methods that are considered active, but by far the most predominate one is ODAS (O = oxidation, DA = dosing with alkali, and S = sedimentation), which is common to that of traditional wastewater treatment plants (USEPA 2000; USEPA 2004). Other active treatment technologies that are occasionally used for AMD, but which are not covered here, include sulfidisation, biosedimentation, sorption and ion exchange, and membrane processes like filtration and reverse osmosis (Younger et al. 2002).

Although the most common order of treatment in industrial wastewater treatment systems is ODAS, for treatment of AMD the most common order is DAOS (Younger et al. 2002). Dosing with alkali (DA) is typically the first step followed by oxidation (O) and sedimentation (S). Oxidation rates for dissolved metals in reduced form such as ferrous iron (Fe\(^{2+}\)) are strongly influenced by pH (Stumm & Morgan 1996), therefore it is beneficial to raise the pH prior to the oxidation step in treatment of AMD. Sometimes a pre-treatment step precedes DAOS such as sedimentation to reduce the concentration of total suspended solids (TSS) which can affect treatment system performance.

A range of factors will influence the selection of appropriate active treatment systems including TSS content, flow rate (L/s), Fe concentration (mg/L), the need for Mn removal, and available land area (Fig. 3). Once an active treatment system has been selected, a computer program such as AMDTreat (Means et al. 2003) can be used to design specific components of the system and to determine potential costs.

**Pretreatment**

Where high suspended solid loads are present, pretreatment of the AMD may be required. High concentrations of TSS can affect treatment system performance through clogging piping and flumes, and damaging pumps. TSS concentrations are typically reduced through sedimentation techniques, such as gravity assisted separation, with the solids recovered as a slurry or sludge. Depending on available land area, gravity assisted separation is accomplished either with clarification or by using settling ponds or sedimentation ponds (Rajaram et al. 2001). In clarification, water flows into the centre of a clarifier tank and then flows slowly and uniformly outward toward the tank walls (USEPA 1983, 2000). The water leaves the clarifier over a weir at the top allowing solids to settle to the bottom of the clarifier. The solids are periodically removed, dewatered and disposed. With settling ponds, sufficient residence time is required for suspended solids to settle out of solution and accumulate at the base of the pond. Depending on the rate of accumulation of solids, sludge is removed periodically from the pond to maintain the necessary residence time.
Dosing with alkali (DA)

The main goal of this step is to add enough neutralising agent to raise the pH and to lower the concentrations of dissolved metals by forming metal hydroxides and oxyhydroxides. The most commonly used chemicals include soda ash or sodium carbonate (Na₂CO₃), hydrated lime or calcium hydroxide (Ca(OH)₂), quicklime or calcium oxide (CaO), caustic soda or sodium hydroxide (NaOH), and ammonia (NH₃) (Skousen et al. 2000). Magnesium oxide or hydroxide (MgO or Mg(OH)₂) and limestone (CaCO₃) are occasionally needed for Mn removal.
used. Selection of an appropriate chemical is primarily dependent on the concentrations of dissolved Mn and Fe and the flow rate of the AMD. Other common metal ions in AMD, such as Al, and to a lesser extent Zn, and Ni, are removed along with Fe, and are not a factor in deciding among the neutralising chemicals. Other factors will also influence chemical selection. These include: chemical cost, neutralising efficiency, maximum pH attainable and therefore ability to remove metals such as Mn, dispensing mechanism required, mixing mechanism required, health and safety issues, sludge settling rates and therefore requirement for flocculants or coagulants, and resulting sludge volume and density (Table 1) (Skousen et al. 2000; Waters et al. 2003; Means 2006).

Chemical cost in particular can be significant, as over the long term the largest single cost component in most systems is the neutralising chemical (Waters et al. 2003). It is recommended to conduct bench scale tests on various chemicals before final selection (Younger et al. 2002) and to conduct a sequential titration acidity analysis as described in Hilton (2004).

Manganese is a difficult metal to remove from solution as it exhibits high solubility over a broad pH range (4.5–8) and the chemical oxidation of Mn is kinetically slow (Bamforth et al. 2006). The most effective way to remove Mn from water is to raise the pH above 9 and allow Mn$^{2+}$ to oxidise to Mn$^{4+}$ or Mn$^{3+}$ and form insoluble Mn oxides or Mn carbonates (Evangelou 1998). Where Mn removal is necessary, the most effective neutralising chemicals for Mn removal are NaOH and NH$_3$ (Skousen et al. 1990, 2000). If NH$_3$ is used, it is recommended to use a pH-driven monitoring system, because over application can lead to toxicity of the treated water. In addition, NaOH shows a nearly linear relationship with pH (to 12) while NH$_3$ shows a logarithmic curve, with only small changes in pH occurring above 9.2 with the addition of more chemical (Skousen et al. 1990). Although Ca-based chemicals can be used for Mn removal, the most commonly used chemicals for Mn removal are NaOH and NH$_3$ (Skousen et al. 1990, 1998). It is not economical to use Ca-based chemicals for Mn removal due to the very long residence times needed to attain a high pH (slower dissolution rates than NaOH and NH$_3$) and the large amounts of unreacted chemical that are produced when raising the pH above 7 (Skousen 1988; Skousen et al. 2000; Means 2006).

Iron concentration is only a factor in treatment selection when considering treatment of very low flow AMD (<1 L/s) where active treatment may be considered as an interim solution or a solution to an intermittent problem. Where Fe is present in low concentrations (<20 mg/L), Na$_2$CO$_3$ dispensed via simple dispensing mechanisms (e.g., wooden box, barrel, or drums with water flowing in and out) is a suitable solution (Skousen et al. 1990; 2000; Means 2006). If Fe concentration is above 20 mg/L, Na$_2$CO$_3$ may still be used although a mixing system should be employed, otherwise another neutralising chemical and different dispensing mechanism may be more appropriate.

In situations where Mn is not a major concern and flow rates are generally above 1 L/s and/or Fe concentration is above 20 mg/L, CaO, or the hydrated form Ca(OH)$_2$, is the most commonly used chemical for neutralisation (Skousen et al. 1990, 2000). Over the long term, especially for high acidity and high flow rates, these are generally the least expensive chemicals for treatment, however, in New Zealand powdered limestone has been shown to be a cost effective solution for high flow and high acidity AMD (Weber et al. 2007, 2008). The dissolution rate of Ca-based compounds such as CaO, or Ca(OH)$_2$ is slower than that of other chemicals, therefore effectiveness and efficiency of treatment are greatly improved by mechanical mixing (Skousen et al. 1990; Rajaram et al. 2001). Rajaram et al. (2001) recommend mechanical mixing above a flow rate of 20 L/s.

**Oxidation (O)**

The goal of the oxidation step is to ensure reduced metals such as Fe$^{2+}$ and Mn$^{2+}$ are oxidised to Fe$^{3+}$ and Mn$^{4+}$ so that they can form hydroxide, oxide, and carbonate precipitates and be removed from solution (Skousen et al. 2000; Younger et al. 2002). This step may not be necessary if the metals are already highly oxidised through the previous treatment step. Bench scale tests at the time of system design would be required to confirm this.

Oxidation is typically undertaken using mechanical aeration, although sometimes chemical oxidation is used. Cost and effectiveness can be used to decide between mechanical and chemical oxidation. Mechanical aeration techniques include stirring with rotating blades (most common), inline venturi aeration, trickle filter aeration (water trickling through a tank filled with high-surface area media and with air bubbled into the water), and cascade aeration (if sufficient land area is available).

Chemical oxidants commonly used include hydrogen peroxide (H$_2$O$_2$), sodium hypochlorite (NaClO), calcium hypochlorite (Ca(ClO)$_2$), and potassium permanganate (KMnO$_4$) (Skousen et al. 1993; Skousen et al. 2000). Another potential oxidant is calcium peroxide (CaO$_2$) which not only can oxygenate AMD but can also neutralise acidity (Skousen et al. 2000). Cost, availability and effectiveness are typically used to decide among the various chemical oxidants.

**Sedimentation (S)**

The final step in the process is sedimentation to remove the metal precipitates formed during the early stages of treatment. The methods used include gravity assisted separation with or without coagulants/flocculants followed by sludge dewatering and disposal. Depending on available land area, gravity assisted separation is accomplished either with clarification or by using settling ponds or sedimentation
ponds. In cases with very high flow rates and/or high-acidities (common in New Zealand), available land area may limit the use of sedimentation ponds. In clarification, the treated AMD flows into the centre of a clarifier tank and then flows slowly and uniformly outward toward the tank walls (USEPA 1983, 2000). The water leaves the clarifier over a weir at the top allowing solids to settle to the bottom of the clarifier. The solids are periodically removed, dewatered and disposed. Several types of clarifiers are used in AMD treatment, including horizontal flow-type clarifiers, upflow solids contact clarifiers, and thickeners (see USEPA 1983 for discussion).

The use of coagulants/flocculants may be necessary when flow rates are > 5 L/s, when residence times in clarifiers or settling ponds can be insufficient for complete metal precipitation. Treatment with calcium hydroxide and sodium carbonate produce a granular, dense floc versus a more gelatinous, loose floc generated from treatment with sodium hydroxide and ammonia (Ackman 1982). Coagulation and flocculation are two separate processes involving addition of chemicals to promote settling of suspended particulates (Bratby 1980; Skousen et al. 1993; Skousen et al. 2000). Both processes enhance sedimentation performance by increasing particle size resulting in increased settling rates.

Coagulation refers to the addition of chemicals to reduce the net electrical repulsive forces at particle surfaces, promoting consolidation of particles. The most commonly used coagulants include aluminium sulphate (Al2(SO4)3), ferric sulphate (Fe2(SO4)3), and ferrous sulphate (FeSO4). Flocculation refers to the addition of chemicals to join particles by bridging the spaces between suspended particles. Flocculants consist of polymer chemicals which adsorb suspended particles onto polymer segments. The most commonly used flocculants include synthetic anionic (negatively-charged surfaces) and cationic (positively-charged surfaces) chemicals and polynaphthylates (both positive and negative charges on surface based on pH).

Coagulants and/or flocculants are usually added in a rapid mix tank or with an in-line mixer and then the wastewater flows to a flocculation basin or tank where slow mixing allows the particles to agglomerate in a more settleable solid. The treated water then flows either into a clarifier or a settling pond for removal of TSS. Bench-scale laboratory experiments are recommended to determine appropriate type and dosage of coagulant/flocculant.

Sludge dewatering and disposal can be a significant cost of AMD treatment, frequently exceeding chemical costs by several times (Skousen et al. 2000). The sludge produced by sedimentation typically contains between 1% and 5% solids. The chemical composition is generally composed of hydrated Fe2+ or Fe3+ oxyhydroxides, CaSO4, Al(OH)3·6H2O, CaCO3, and Ca(HCO3)2 with trace amounts of Si, PO4, Mn, Cu and Zn (Ackman 1982). They are dewatered using pressure, vacuum or, rarely, centrifugal force. Alternatively, sludge can be pumped from settling ponds directly into deep coal mines on a periodic basis or, if possible, ponds can be constructed with enough capacity to hold sludge for a number of years (case studies in Brown et al. 1994a). The most common dewatering methods are plate and frame pressure filtration, belt pressure filtration and vacuum filtration. A plate and frame filter press can produce the driest filter cake, followed by the belt press, and lastly, the vacuum filter (USEPA 2000).

Disposition of filter cake (dewatered sludge) is usually to an off-site landfill, incineration facility or appropriate area for land application. If the sludge is non-toxic, filter cake from the active treatment process can sometimes be disposed of on site, or as mentioned above, pumped directly into deep mines with little to no dewatering. See Brown et al. (1994a, b, c) for information on volume, stability, and composition of sludge generated from active treatment of AMD.

**Passive treatment**

**Passive remediation strategies**

Remediation of AMD using passive remediation technologies can be placed into two broad categories: oxidising and reducing strategies (Table 2) (Trumm et al. 2003; Trumm et al. 2005). AMD is generated through an oxidation process, which results in the dominant contaminant, Fe, being present in two states, ferrous (Fe2+) and ferric (Fe3+) (Singer & Stumm 1970). Oxidising systems remove Fe from the AMD by continuing the oxidation process such that all Fe2+ is oxidised to Fe3+, and once the pH has been raised sufficiently, precipitated out of the AMD as ferric hydroxide (Fe(OH)3). For reducing systems, the AMD oxidation process is reversed, such that Fe and sulphate are reduced, forming the compounds FeS2, FeS, and H2S, thus also removing dissolved Fe and sulphate from the AMD.

Typical remediation systems that employ the oxidising strategy are open limestone channels (OLCs) (Ziemkiewicz et al. 1994), open limestone drains (OLDs) (Cravotta & Trahan 1999), limestone leaching beds (LLBs) (Black et al. 1999), slag leaching beds (SLBs) (Simmons et al. 2002), and diversion wells (DWs) (Arnold 1991). OLCs and DWs typically require a steep topography in order to generate the necessary aeration and to prevent armouring of limestone by metal hydroxides, which can inhibit the dissolution of limestone (Ziemkiewicz et al. 1997).

Typical remediation systems that employ the reducing strategy are anaerobic wetlands (Skousen et al. 2000; PIARIMID Consortium 2003; O’Sullivan 2005), anoxic limestone drains (ALDs) (Hedin & Watzlaf 1994), bacteria-based sulphate-reducing bioreactors (SRBRs) (Mattes et al. 2007), also known as biogeochemical reactors (BGCRs), and successive alkalinity producing systems (SAPS) (Kepler & McCleary 1994), also known as vertical flow wetlands (VFWs) or reducing and alkalinity producing systems (RAPS) (Zipper & Jage 2001).
The choice between the two strategies is typically based on the water chemistry (largely dissolved oxygen (DO) content and Fe\(^{2+}/Fe^{3+}\) ratio). For AMD which is highly oxidised (DO level at saturation and all Fe as Fe\(^{3+}\)) the oxidising strategy is most appropriate; for AMD with low DO and all Fe as Fe\(^{2+}\), the reducing strategy is usually recommended. However, site limitations, such as available land area, climate and topography, may limit the use of certain systems.

Flow chart
Parameters necessary to use the flow charts prepared by Hedin & Nairn (1992), Skousen et al. (1999), and Skousen et al. (2000) include water chemistry (DO content, Fe\(^{2+}/Fe^{3+}\) ratio, Al concentration and pH) and flow rate. Topography and available land area are not included among the parameters. However, on the West Coast of New Zealand, these parameters may limit choice between systems. Very steep topography, dense and often protected vegetation, and a high-rainfall climate result in AMD with very high and variable flow rates in locations with very limited space for remediation. Flow charts have been prepared here more specifically for New Zealand AMD sites incorporating site parameters of AMD chemistry (Fe concentration, Al concentration, Fe\(^{2+}/Fe^{3+}\) ratio and DO), site topography and available land area (Fig. 4).

As discussed earlier, due to the highly variable flow rates at many AMD sites in New Zealand, treatment systems may only be able to treat base flow conditions rather than total flow. Equalisation header ponds can dampen peak flows to some extent, but systems need to accommodate these high flows either through a bypass or by designing systems to handle high flows. Before these decisions are made, however, the effect of storm events on flow rate versus acidity should be quantified. The common variables in New Zealand of steep topography coupled with high flow rates are particularly suitable for three passive treatment systems: steep OLCs, DWs, and limestone sand dosing.

Iron concentration
Iron is the most difficult metal to remove from AMD using passive treatment technology, largely due to coating or armouring of limestone, the most commonly used neutralising agent, by Fe oxides and oxyhydroxides (Hilton 2005). This armouring reduces the dissolution rate of the limestone and hence, neutralisation of the AMD (Ziemkiewicz et al. 1997; Watzlaf et al. 2000b; Hammarstrom et al. 2003). Much of the current research into passive treatment continues to try to find ways to treat AMD without significant armouring occurring. In addition, Nairn et al. (1991) and Robbins et al. (1999) show that high levels of sulphate (>1500 mg/L) can result in precipitation of gypsum and Hammarstrom et al. (2003) show that gypsum can also armour limestone and reduce the dissolution rate.

The flow chart (Fig. 4) is split into a high Fe concentration section and a low Fe concentration section, with the high Fe section further split into a reduced AMD (most Fe as Fe\(^{2+}\), DO<20%) and an oxidised AMD (most Fe as Fe\(^{3+}\), DO>20%). The reduced AMD represents a special case as Fe\(^{2+}\) will remain in solution even at high pH as long as the DO remains low (Stumm & Morgan 1996). If the land area is suitable, the best treatment option in this case is an ALD, since high alkalinity can be generated with no Fe precipitating, and as the treated AMD leaves the ALD, oxidation occurs and Fe\(^{2+}\) readily oxidises to Fe\(^{3+}\) and precipitates as oxides and oxyhydroxides in a settling pond (Hedin & Watzlaf 1994). High Al concentrations, however, can affect performance of ALDs (see following section). Ziemkiewicz et al. (2003) found that ALDs were one of three types of systems over the long term that consistently provided a high level of reliability, high acid load removal, and low treatment cost. If the land area is not suitable for an ALD, reducing systems such as VFWs or anaerobic wetlands can be selected. As the AMD is already in a reduced state, continued reduction and formation of sulphides will occur in these systems.

For AMD with high concentrations of Fe and most of the Fe in the oxidised state, either oxidising or reducing systems may work, and selection of potential systems may be constrained by available land area. OLCs are best constructed on steep slopes ( > 20%) to minimise armouring (Ziemkiewicz et al. 1997), otherwise access should be available for a bulldozer to break up armoured limestone periodically. Diversion wells (Arnold 1991), limestone dosing (Mills 1996; Zurbuch 1996; Weber et al. 2007), and SLBs can also work well with high Fe concentrations. Alternatively, reducing systems such as VFWs or anaerobic wetlands can work if the residence time is very long in the organic layers to ensure DO concentrations are lowered and Fe\(^{3+}\) is reduced back to Fe\(^{2+}\) and sulphate is reduced to sulphide prior to contact with limestone. Both systems must be constructed with a large holding capacity for precipitated sulphides.

AMD with relatively low Fe concentrations ( <10 mg/L and more ideally less than 5 mg/L) can be treated with either oxidising or reducing systems. Aluminium concentrations, DO, and land area are used to further decide between remediation strategies and passive treatment systems.

Aluminium concentration
Aluminium is a much less problematic metal than Fe in the treatment of AMD. It precipitates out of solution as an amorphous white slime composed of Al oxyhydroxide and hydroxysulfate at around a pH of 5 (Bigham 1994; Nordstrom & Alpers 1999), and it does not coat or armour limestone to the same extent as Fe (Hammarstrom et al. 2003; Trumm et al. 2008).
Fig. 4 Flow chart to select among AMD passive treatment systems.
The reduced AMD (DO < 20%) represents a special case, as discussed above, in which an ALD is the preferred treatment solution. Aluminium, however, will precipitate in the ALD and, if the concentration is too high, will tend to reduce the permeability of the drain with time, potentially leading to eventual failure. Skousen et al. (2000) recommend a maximum Al concentration of 25 mg/L, but Watzlaf et al. (2000b) found ALDs could fail with Al concentrations above 21 mg/L, and Watzlaf et al. (2003) recommend Al concentrations below 1 mg/L as an extra precaution against failure. It is recommended that ALDs can be used with Al concentrations up to 25 mg/L but extra permeability should be built into the ALD at the higher values. If the land area is not suitable for an ALD, an anaerobic wetland can be selected. As the AMD is already in a reduced state, continued reduction and formation of sulphides will occur in these systems.

For low Al concentrations but highly oxidised AMD, either oxidising or reducing systems can be used depending on available land area. If reducing systems are used, residence times must be long enough to ensure DO concentrations are lowered and any remaining Fe is reduced to sulphides. Aluminium precipitates that build up in VFWs are periodically flushed into a settling pond (Danehy et al. 2002).

AMD with high Al concentrations ( > 25 mg/L) should be treated using an oxidising system. If a reducing system is used, Al oxyhydroxide and hydroxysulfate precipitates will eventually reduce permeability and can cause the system to fail. Even with concentrations as high as 56 mg/L, oxidising systems such as an LLB are adequate for treatment (Hilton et al. 2003).

Dissolved oxygen concentration
Dissolved oxygen content indicates the degree to which the AMD is oxidised. In general, a highly reduced AMD (DO < 20%) is best treated using a reducing strategy whereas an oxidised AMD (DO > 20%) is best treated using an oxidising strategy. However, available land area may limit choice of remediation system. If a reducing strategy is attempted on a highly oxidised AMD, only VFWs and anaerobic wetlands are suggested and a long residence time in the organic layer is recommended to ensure complete removal of DO and reducing conditions to establish. Oxidising strategies can be used for AMD with low DO concentrations. However, these systems should be constructed with cascades to add DO to enable oxidation reactions to occur.

Available land area
Available land area descriptions are limited to steep vs. not steep topography and large flat area vs. long narrow area. Steep topography is generally suitable for oxidising systems such as diversion wells, OLCs and limestone sand dosing where turbulence can help minimise armouring of limestone by Fe oxides and oxyhydroxides (Mills 1996; Zurbuch 1996; Ziemkiewicz et al. 1997). Long narrow areas are suitable for ALDs (reducing system) and OLCs (oxidising system) but if an OLC is constructed with a low gradient, Fe will armour the limestone if it is present in significant amounts. Large flat areas are suitable for both reducing systems (VFWs and anaerobic wetlands) and oxidising systems (LLBs and SLBs).

Once potential treatment solutions have been identified through the use of the flow chart, it is recommended that small-scale trials be constructed on site to test the effectiveness of the various options before investing in full-scale system construction (see Trumm et al. 2006 and Trumm et al. 2008 for examples of small scale trials). Ecotoxicity experiments should be conducted using treated water to verify treatment will enable restoration of the aquatic ecosystem, and system autopsies should be performed to verify system performance parameters and system longevity. The choice of the full-scale system should be based on the results of the field trials and a review of the cost, effectiveness and limitations for each option (Table 2). Full scale systems can be designed using the computer program AMDTreat (Means et al. 2003).

New Zealand case studies
The process of passive treatment selection using the flow chart presented in this paper (Fig. 4) has been tested at several sites in New Zealand. RAPS were trialled at the Pike River Adit AMD and Sullivan Mine AMD sites and a limestone leaching column experiment to simulate an LLB was trialled on the Blackball Mine AMD (Trumm & Watts 2010). Positive results at the Pike River Adit resulted in the construction of a full-scale RAPS, and a large-scale RAPS trial is planned for the Sullivan Mine AMD. A RAPS, OLC, and LLB were trialled at the Herbert Stream site on the Stockton Mine (Trumm et al. 2008), resulting in a design for a full-scale LLB for the site. In each case, land area constraints narrowed the choice of passive treatment system, and flow rates factored in the design of full-scale systems.

Conclusions
Treatment of AMD is accomplished by either active or passive treatment systems. System selection is often critical for treatment success. The work presented here includes three flow charts to help select between active and passive treatment, and to select the optimal system type within each category. To select between active and passive treatment, site parameters of pH, acidity, flow rate, and acid load are necessary. To select among the active treatment options, site parameters of suspended solids content, Fe and Mn...
concentrations, flow rate and available land area are used. Previous workers have identified the major parameters necessary for passive treatment selection. The flow chart presented here uses some of these parameters (Fe and Al concentrations, \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ratio, and DO) in conjunction with important parameters for application to New Zealand sites: topography, climate and available land area. Topography at AMD sites in New Zealand is often steep with limited space for remediation systems. Therefore, treatment selection may be restricted by topography and land area as well as AMD chemistry. Prior to full scale construction, for active treatment solutions it is recommended to conduct bench scale tests on various chemicals, to complete a sequential titration acidity analysis, and to review cost, effectiveness, limitations and risk of failure for various options. For passive treatment solutions it is recommended that small-scale trials be conducted on site to verify optimal treatment selection.

Acknowledgements
This research was financed by the New Zealand Foundation for Science, Research and Technology (contract CRLX0401). The author would like to acknowledge the helpful comments from Jo Cavanagh on earlier drafts of the text and flow charts. The author would also like to acknowledge the helpful comments of two anonymous reviewers.

References


Acid mine drainage treatment flow charts


