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

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ABSTRACT
Treatment of acid mine drainage (AMD) 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 systems are more commonly used at active mines whereas passive treatment systems are typically used at closed and abandoned mines. Active mines often have limited space for remediation systems and have drainage chemistry and flow rates that can change as mining proceeds, factors that are addressed more easily with active treatment than passive treatment. However, if sufficient space is available, and chemistry and flow rates are not expected to change significantly with time, passive treatment can be a suitable solution at active mines. In the long term, passive treatment is more economic 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 typically not included a variable important at New Zealand AMD sites: topography and available land area. Very steep topography, dense and often protected vegetation, and a high-rainfall climate result in AMD with high flow rates in locations with limited space for remediation. Flow charts specific to New Zealand have been prepared which accommodate topography and available land area. Parameters necessary to use the flow charts include suspended solids content, pH, selected metal concentrations (iron, aluminium, and manganese), ferrous to ferric iron ratio, acidity, dissolved oxygen concentration, flow rate, acid load, topography, and available land area.

Additional Key Words: acid mine drainage, iron, aluminium, manganese, remediation

INTRODUCTION
AMD treatment can be accomplished by either active or passive techniques (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 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. 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 systems typically require continuous dosing with chemicals, consume power and require regular operation and maintenance, but they are very reliable. Their main advantages are they are very effective at removal of contaminants from mine drainage, have precise process control such that they can be engineered and operated to produce a specific water chemistry, and they can be accommodated in locations where only a small land area is available. 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 a treatment system.

Passive systems rely on natural physical, geochemical and biological processes but can fail if not carefully selected and designed (Skousen et al., 2000). 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 typically more economic than using active systems especially after mine closure (Skousen and Ziemkiewicz, 2005). AMD at closed and abandoned mines typically 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.

There are a number of factors that can influence the decision as to whether to use active or passive treatment (Figure 1).

ACTIVE TREATMENT
Active treatment for AMD is largely based on industrial wastewater treatment technologies (Younger et al., 2002). There are a variety of methods that are considered active, but by far the most predominate one is ODAS (oxidation, dosing with alkali, and sedimentation), which is common to that of traditional wastewater treatment plants (USEPA, 2000; USEPA, 2004).

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 is typically the first step followed by oxidation and sedimentation. Oxidation rates for dissolved metals in reduced form such as Fe$^{2+}$ are strongly influenced by pH (Stumm and Morgan, 1996), therefore it is beneficial to raise the pH prior to the oxidation step in treatment of AMD. Sometimes a pretreatment 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, Mn concentration (mg/L), flow rate (L/s), Fe concentration (mg/L), and available land area (Figure 2). 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.
Selection of an appropriate chemical is primarily dependent on the concentrations of dissolved Mn and Fe and the flow rate of the AMD, although 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).

PASSIVE TREATMENT

Passive Remediation Strategies

Remediation of AMD using passive remediation technologies can be placed into two broad categories: oxidising and reducing strategies (Trumm et al., 2003; Trumm et al., 2005). AMD is generated through an oxidation process, which results in the dominant contaminant, iron, being present in two states, ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$; Singer and Stumm, 1970). Oxidising systems remove iron from the AMD by continuing the oxidation process such that all ferrous iron is oxidised to ferric iron, 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 iron cations and sulphate are reduced, forming the compounds FeS$_2$, FeS, and H$_2$S, thus removing dissolved iron and sulphate from the AMD.

Typical remediation systems that employ the oxidising strategy are open limestone channels (OLCs), open limestone drains (OLDs), limestone leaching beds (LLBs), slag leaching beds (SLBs), and diversion wells (DWs; Anonymous, 2001). 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 (Anonymous, 2001), anoxic limestone drains (ALDs; Hedin and Watzlaf, 1994), sulphate-reducing bioreactors, and successive alkalinity producing systems (SAPS), also known as vertical flow wetlands (VFWs) or reducing and alkalinity producing systems (RAPS; Zipper and Jage, 2001).

Figure 2. Flow chart to design a site-specific active treatment system for AMD (modified from Rajaram et al., 2001).
Table 1: Table of characteristic 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>Neutarlisation efficiency (%)</th>
<th>Conversion Factor (mass needed compared to limestone)</th>
<th>Cost of Chemical (relative to NaOH)</th>
<th>Dispensing Mechanism</th>
<th>Key benefits</th>
<th>Key limitations</th>
<th>Risk of failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda ash or sodium carbonate (Na₂CO₃)</td>
<td>11.6</td>
<td>95 - 100 (powder) 60 (briquettes)</td>
<td>1.06</td>
<td>0.56</td>
<td>Briquettes placed in wooden box or 55 gallon drum in AMD stream</td>
<td>High efficiency in powder form, most metals precipitate, low sludge volumes</td>
<td>Health and safety issues, poor sludge settling rates, potential sodium toxicity</td>
<td>Potential for reduced treatment effectiveness when using briquettes if acidity loading rates increase significantly (most commonly seen as an interim treatment or only for low flow/low acidity AMD)</td>
</tr>
<tr>
<td>Hydrated lime or calcium hydroxide (Ca(OH)₂)</td>
<td>12.4 - 12.5</td>
<td>90 - 95</td>
<td>0.74</td>
<td>0.17</td>
<td>Silo or hopper with mechanical feed screw to dispense powder. Batching tank to mix powder with water. Can use aqueous slurry. Mixing suggested.</td>
<td>High efficiency, most metals precipitate, low cost, widely available</td>
<td>Health and safety issues, reagent saturation can lower efficiency</td>
<td>If acidity loading rates increase beyond system capacity to neutralise and settle hydroxides, treatment effectiveness will drop. Poor maintenance can result in plugged dispensing mechanism and complete failure.</td>
</tr>
<tr>
<td>Quicklime or calcium oxide (CaO)</td>
<td>12.4 - 12.5</td>
<td>90</td>
<td>0.56</td>
<td>0.11</td>
<td>Silo or hopper with mechanical feed screw to dispense powder or water wheel feeder with 1 ton storage bin (no power). Batching tank to mix powder with water. Mixing suggested.</td>
<td>High efficiency, most metals precipitate, very low cost, widely available</td>
<td>Health and safety issues, reagent saturation can lower efficiency, possible sumping of pebbles</td>
<td>If acidity loading rates increase beyond system capacity to neutralise and settle hydroxides, treatment effectiveness will drop. Poor maintenance can result in plugged dispensing mechanism and complete failure. Must be watertight or will hydrate and form calcium hydroxide and plug dispensing mechanism.</td>
</tr>
<tr>
<td>Ammonia (NH₃ or NH₄OH)</td>
<td>9.2</td>
<td>100</td>
<td>0.34</td>
<td>0.60</td>
<td>Compressed and stored as liquid in tank, gas injected near bottom of pond or water inlet. No mixing required.</td>
<td>Very high efficiency, most metals precipitate, low sludge volumes</td>
<td>Health and safety issues, poor sludge settling rates, can be toxic to aquatic life, high cost</td>
<td>If acidity loading rates increase beyond system capacity to neutralise and settle hydroxides, treatment effectiveness will drop.</td>
</tr>
<tr>
<td>Caustic soda or sodium hydroxide (NaOH)</td>
<td>14</td>
<td>100</td>
<td>0.80 (solid)</td>
<td>1</td>
<td>Stored as a liquid in tank, dispense through metering pump or valve and feeder hose near top of pond or water inlet. No mixing required.</td>
<td>Very high efficiency, most metals precipitate, low sludge volumes</td>
<td>Health and safety issues, poor sludge settling rates, potential sodium toxicity, highest cost of all chemicals, low freezing point</td>
<td>If acidity loading rates increase beyond system capacity to neutralise and settle hydroxides, treatment effectiveness will drop.</td>
</tr>
<tr>
<td>Magnesium oxide or hydroxide (MgO or Mg(OH)₂)</td>
<td>Theoretical: 10.2</td>
<td>90 - 95</td>
<td>0.40 or 0.58</td>
<td>0.22</td>
<td>Silo or hopper with mechanical feed screw to dispense powder. Batching tank to mix powder with water. Mixing suggested.</td>
<td>Very high efficiency, most metals precipitate, low sludge volumes, low cost</td>
<td>Some health and safety issues, not widely available, lower reaction rate than calcium hydroxide</td>
<td>If acidity loading rates increase beyond system capacity to neutralise and settle hydroxides, treatment effectiveness will drop.</td>
</tr>
<tr>
<td>Limestone (CaCO₃)</td>
<td>Theoretical: 9.4</td>
<td>30 - 90</td>
<td>1</td>
<td>0.04</td>
<td>Silo or hopper with mechanical feed screw to dispense powder. Batching tank to mix powder with water. Mixing suggested.</td>
<td>Safe to use, lowest cost of all chemicals, readily available, cannot overheat</td>
<td>Low efficiency, not all metals removed (ineffective for Mn), ammonium</td>
<td>If acidity loading rates increase beyond system capacity to neutralise and settle hydroxides, treatment effectiveness will drop.</td>
</tr>
</tbody>
</table>
The choice between the two strategies is typically based on the water chemistry (largely DO content and ferrous/ferric ($\text{Fe}^{2+}/\text{Fe}^{3+}$) iron ratio). For AMD which is highly oxidised (DO level at saturation and all iron as ferric iron) the oxidising strategy is most appropriate; for AMD with low DO and all iron as ferrous, the reducing strategy is usually recommended. However, site limitations, such as available land area and topography, may limit the use of certain systems.

**Flow Chart**
Parameters necessary to use the flow charts prepared by Hedin and Nairn (1992), Skousen et al. (1999), and Skousen et al. (2000) include water chemistry (DO content, ferrous/ferric iron ratio, aluminium concentration and pH), and flow rate. Topography and available land area are not included among the parameters, however, on the West Coast in New Zealand, these parameters may limit choice between systems. Very steep topography, dense and often protected vegetation (and animals such as snails), and a high-rainfall climate result in AMD with very high flow rates in locations with very limited space for remediation. Flow charts have been prepared for New Zealand AMD sites incorporating site parameters of AMD chemistry (Fe concentration, Al concentration, ferrous/ferric iron ratio and DO), site topography and available land area (Figure 3). One full-scale remediation system has been installed in New Zealand based on this methodology (SAPS unit at the Pike River Adit based on the results of the field trials documented in Trumm et al., 2006) and another is planned (LLB unit at the Herbert Stream based on the results of the field trials documented in Trumm et al., 2008).

**Fe Concentration**
Iron is the most difficult metal to remove from AMD using passive treatment technology, largely due to coating or armouring of limestone by Fe oxides and oxyhydroxides which reduces the dissolution rate of the limestone and hence, neutralisation of the AMD (Ziemkiewicz et al., 1997; Watzlaf et al., 2000; Hammarstrom et al., 2003; Hilton, 2005).

**Al 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 and Alpers, 1999), and it does not coat or armour limestone to the same extent as Fe (Hammarstrom et al., 2003; Trumm et al., 2008).

**Dissolved oxygen concentration**
DO content indicates the degree to which the AMD is oxidised. 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**

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 (Ziemkiewicz et al., 1997; Mills, 1996; Zurbuch, 1996). 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 (limestone leach beds and slag leach beds).

Figure 3. Flow chart to select among AMD passive treatment systems.
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, limitations and risk of failure for each option.

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, flow rate, acidity, 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, ferrous/ferric iron ratio, and DO) in conjunction with two important parameters to New Zealand: topography 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.

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REFERENCES


