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A Summary of Passive and Active Treatment Technologies for Acid and Metalliferous Drainage (AMD)

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ABSTRACT

A broad range of technologies is available for the treatment of Acid and Metalliferous Drainage (AMD). These technologies utilise one or a combination of chemical, physical and biological processes, including pH control, adsorption/absorption, complexation, chelation, biological mediation, oxidation/reduction, electrochemistry, sedimentation, flocculation/filtration/settling, ion exchange and crystallisation. By far the most common process for treating AMD is via pH control.

The selection of an appropriate treatment system requires an understanding of the "Acidity", flow rate and "Acidity Load" (ie. the product of Acidity and flow rate) of the AMD that needs to be treated. AMD treatment systems can be broadly categorised as either "passive" or "active" systems, which differ according to their ability to handle Acidity, flow rate and Acidity Load of the influent AMD. Most passive and active systems utilise aggregate carbonate to neutralise the pH and encourage precipitation of metals as hydroxides or sulphide minerals. In addition, passive treatment systems often use organic matter to provide alkalinity and create reducing conditions which favour the precipitation of metal sulphides.

Passive treatment systems are best suited to AMD with low Acidity (<800 mg CaCO₃/L), low flow rates (<50 L/s) and therefore low Acidity Loads (<100-150 kg CaCO₃/day). Passive treatment systems include Open/Oxic Limestone Drains, Anoxic Limestone Drains, Limestone Diversion Wells, Pyrolusite® Limestone Beds, aerobic and anaerobic Wetlands, a range of Reducing and Alkalinity Producing Systems, Permeable Reactive Barriers, Slag Leach Beds, sulphide passivation/micro-encapsulation, electrochemical covers, alkalinity producing covers and Gas Redox and Displacement Systems (GaRDS).

Unlike their passive counterparts, active treatment systems can be engineered to accommodate essentially any Acidity, flow rate and Acidity Load. Although not limited by tight operational parameters as in the case of passive systems, economic considerations play a significant role in determining the viability of active treatment systems. Active treatment of AMD can be achieved using fixed plants or portable equipment for *in-situ* treatment. Fixed plants include Low Density and High Density Sludge (LDS and HDS) plants, Pulsed Carbonate Reactors, Microbial Reactor Systems and crystallisation plants. A number of *in-situ* water-based or land-based treatment systems are also available, including the Neutra-Mill, Calibrated Reagent Applying Blender (CRAB), Aqua-fix and Hydro-Active Limestone Treatment (HALT) systems. *In-situ* treatment becomes a viable option when the cost of diverting AMD to a fixed plant exceeds the cost of building a smaller, portable plant.

It is evident that regardless of emerging technologies, pH control with cost-effective neutralisation reagents will remain the most widely used and lowest cost approach to both passive and active AMD treatment. Active treatment using calcium-based reagents (particularly limestone) is likely to remain the prime choice for neutralising AMD due to the non-proprietary nature of these reagents, their widespread availability, ease of application and cost-effectiveness.

1. Background

Acid and Metalliferous Drainage (AMD) is a major issue affecting both the environment and the economics of metal and coal mining operations worldwide (Plates 1 and 2). In Australia, acid drainage is traditionally referred to as “acid mine drainage” or “acid rock drainage”. The term AMD in this paper encompasses acid (ie. low pH) drainage formed by sulphide oxidation resulting from mining activities, as well as metalliferous drainage, which may have a near-neutral or acidic pH. Near-neutral metalliferous drainage can result from sulphide oxidation and acid production, with subsequent modification of the pH due to partial neutralisation of the acid with some carbonate minerals. At near neutral pH values, several metals can remain in solution. While the impacts of low pH waters can be immediate and severe, near neutral and metalliferous drainage can also have direct impacts associated with the toxicity of elevated metal concentrations. In addition, metalliferous water can have indirect impacts associated with latent acid production via the hydrolysis of dissolved metals.

1.1 Potential Economic and Environmental Impacts of AMD

AMD can have significant impacts on the economics of a mining operation. This is due to the corrosive effects of acid water on infrastructure and equipment, the limitations it places on water reuse and discharge, and the expense incurred implementing effective closure options.

Likewise, AMD has significant potential to cause long term environmental impacts. This is largely due to a decrease in pH and/or elevated heavy metal concentrations in nearby water and soils. AMD can have extreme impacts on the ecology of streams, affecting the beneficial use of waterways downstream of mining operations.

The generation of AMD can:

- Mobilise (bring into solution) metals to levels injurious to aquatic ecosystems, riparian communities and possibly human health (eg. zinc, cadmium, aluminium, copper).
- Limit the downstream beneficial uses of receiving waters (eg. stock, recreation, fishing, aquaculture, irrigation).
- Alter important life supporting balances in water chemistry (eg. bicarbonate buffering system).
- Lead to the development of chemical precipitates (eg. ferric hydroxide, aluminium hydroxide, etc.) that can smother aquatic habitat and reduce light penetration.
- Impact on downstream riparian communities (eg. tree deaths).
- Impact on groundwater quality (particularly shallow aquifers).

AMD can also cause revegetation and rehabilitation difficulties. For example, AMD in soils can lead to significant excesses and deficiencies of key elements for plant growth and difficulties in stabilising mine wastes. Soils contaminated by AMD are at best a significant limitation on vegetation types that can be used for rehabilitation and at worst responsible for a failed rehabilitation plan.



Plates 1-2. Acid and metalliferous drainage (AMD) can have significant economic implications as well as long term environmental impacts at metal and coal mine sites around the world.



1.2 Objectives of AMD Treatment

Treatment of AMD is potentially a costly part of mining operations and a long term liability if not managed correctly. Therefore, it is best practice to avoid and minimise AMD and only treat (as a third priority) when other approaches have failed. Treatment of AMD may be required for:

- Downstream water use or ecosystem protection (to achieve compliance with discharge, surface or groundwater quality criteria).
- Reuse of water on-site (eg. process water to lower operating costs).
- Protection of process-critical and/or expensive on-site infrastructure (ie. to lower operating costs).

The “do it once, do it right” philosophy advocates choosing the right approach/technology, and implementing the chosen system correctly the first time. No single treatment approach can provide a totally walk-away solution, with all systems requiring a degree of monitoring and maintenance. The most suitable approach virtually always depends on site-specific conditions. Selection of an appropriate AMD treatment method also involves quantification of treatment objectives to determine the final use of the treated water. Depending on site-specific objectives, the treatment of AMD can require vastly different tasks requiring significantly different technologies.



1.3 Understanding “Acid”, “Acidity” and “Acidity Load”

Understanding the difference between “acid”, “Acidity” and “Acidity Load” is important for quantifying AMD treatment requirements, and therefore choosing appropriate treatment systems.

“Acid” is a measure of hydrogen ion (H^+) concentration which is generally expressed as pH ($pH = -\log_{10}[H^+]$), whereas “Acidity” is a measure of both hydrogen ion concentration and mineral (or latent) Acidity. Mineral or latent Acidity considers the potential concentration of hydrogen ions that could be generated by the precipitation of various metal hydroxides in solution at a given pH (such as for ferric hydroxide ($Fe(OH)_3$) as shown in Reaction 1c below). It is not unusual for AMD to contain iron (Fe), aluminium (Al), manganese (Mn), copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni) and other metals, and some of these metals can remain in dissolved form even in near neutral solutions. As such, it is possible to have AMD with an elevated Acidity but neutral pH values. In general, Acidity increases as pH decreases (ie. H^+ concentration increases), but there is not always a direct relationship between Acidity and pH. It is therefore important to quantify the contributions of both hydrogen ion concentrations (“acid”) and mineral contributions (“latent” Acidity), in order to determine the total “Acidity” (ie. “acid” + “latent” Acidity) of a stream or water body. Acidity is generally expressed as “mass $CaCO_3$ equivalent per unit volume” (ie. mg $CaCO_3$ / litre).

“Acidity Load” refers to the product of the total “Acidity” (ie. “acid” + “latent” Acidity) and flow rate (or volume) and is essentially equivalent to “ideal” treatment requirements expressed as “mass $CaCO_3$ equivalent per unit time” (or mass $CaCO_3$ equivalent for a given volume of water). Other factors such as reagent purity and dosing efficiency also need to be considered when estimating AMD treatment requirements.

“Acid” can be easily measured in the field using a calibrated handheld pH meter. Estimates of “Acidity” can be measured in a laboratory or estimated from water quality data using a formula such as Equation 1, which is suitable for coal mine drainage¹. If more detailed input water quality data is available, shareware such as ABATES² may be used to obtain “Acidity” estimates. If flow rate or volume data is available, then the measured or estimated “Acidity” values can be converted into “Acidity Load” as shown in Equation 2, or using the ABATES shareware.

¹ Equation 1 is applicable to sites such as coal mines where Fe, Al and Mn represent the dominant components of “Acidity”.

² ABATES is a spreadsheet-based tool that assists with the characterisation and management of AMD. The software can be freely downloaded from www.earthsystems.com.au/tools.htm.



$$\begin{aligned} \text{Acidity (mg/L CaCO}_3) &= 50 \times \{ 3 \times [\text{Fe}^{3+} + \text{Fe}^{2+}] / 56 \\ &\quad + 3 \times [\text{Al}^{3+}] / 27 \\ &\quad + 2 \times [\text{Mn}^{2+}] / 55 \\ &\quad + 1000 \times 10^{-(\text{pH})} \} \end{aligned} \quad \text{(Equation 1)}$$

Note: [] denotes concentration, mg/L

$$\begin{aligned} \text{Acidity load (tonnes CaCO}_3/\text{day)} &= 10^{-9} \times 86,400 \text{ (conversion factor)} \\ &\quad \times \text{Flow rate (L/s)} \\ &\quad \times \text{Acidity (mg/L CaCO}_3) \end{aligned} \quad \text{(Equation 2a)}$$

or...

$$\begin{aligned} \text{Acidity load (tonnes CaCO}_3) &= 10^{-9} \text{ (conversion factor)} \\ &\quad \times \text{Volume (L)} \times \text{Acidity (mg/L CaCO}_3) \end{aligned} \quad \text{(Equation 2b)}$$

1.4 “Acid” Forming and “Acidity” Forming Minerals

AMD is formed when rocks containing sulphide minerals such as pyrite are exposed to air and water, under natural conditions or as a result of human activity (eg. mining), and subsequently leached. The resulting drainage is a near neutral or low pH solution of dissolved metals and sulphate-rich water.

Some minerals are “acid” forming, while others are “Acidity” forming, resulting in “acid and metalliferous” and “near-neutral metalliferous” drainage, respectively.

Pyrite (FeS_2) and marcasite (FeS_2) are the predominant “acid” forming sulphide minerals present in mining situations, with other important metal sulphides including pyrrhotite (FeS), chalcopyrite (CuFeS_2), and arsenopyrite (FeAsS).

“Acidity” forming minerals include sphalerite (ZnS), galena (PbS), chalcocite (Cu_2S) and covellite (CuS).

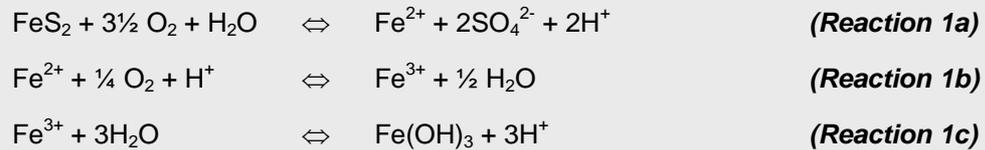
1.5 Chemistry of AMD

The production of acid (H^+) via iron sulphide (eg. pyrite) oxidation can be represented by the following general reaction:





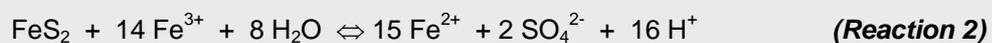
The following more detailed reactions demonstrate the key steps in the acid (H^+) forming process, and highlight the importance of ferric hydroxide ($Fe(OH)_3$) precipitation in the generation of "latent" Acidity ($3H^+$), as shown in Reaction 1c.



When pyrite is exposed to air and water, it decomposes into water-soluble components, including ferrous iron (Fe^{2+}) and sulphate (SO_4^{2-}); 2 moles of acid (H^+) are produced (Reaction 1a). The relatively reduced water-soluble components are further oxidised to form ferric iron (Fe^{3+}) and water; 1 mole of acid (H^+) is consumed (Reaction 1b). This reaction is considered to be the rate-determining step as the reaction rate is pH dependent and proceeds slowly under acid conditions (pH 2-3). Certain Fe-oxidising bacteria can accelerate this reaction, although in many cases, oxidation of Fe^{2+} to Fe^{3+} may only proceed after the mine water has travelled several kilometres off site. The formation of ferric iron (Fe^{3+}) in water results in the hydrolysis of iron to form ferric hydroxide, $Fe(OH)_3$ (an orange precipitate) and 3 moles of acid (H^+) (Reaction 1c).

Ferric hydroxide only precipitates from water in equilibrium with atmospheric oxygen (and with pH above 3.3) after it has been bacterially catalysed or sufficiently aerated / oxidised to facilitate the conversion of soluble ferrous iron to soluble ferric iron. As can be seen in Reaction 1c, the precipitation of $Fe(OH)_3$ is a key acid producing stage. Once sulphides have been oxidised to sulphates (Reaction 1a), it is extremely difficult to avoid oxidation of aqueous ferrous species to ferric species (Reaction 1b) and subsequent hydroxide precipitation (Reaction 1c).

With the formation of aqueous ferric iron (Fe^{3+}) in the presence of fresh iron sulphide, further sulphide oxidation can be accelerated, as represented in the following reaction:



Iron sulphides in geologic materials that are located below the water table remain essentially stable, since the potential for oxidation is limited³. However, where sulphidic materials are exposed to oxidising conditions (air), the iron sulphides react and water can transport the

³ The concentration of dissolved oxygen in natural waters is approximately 25,000 times lower than found in the atmosphere.



reaction products (eg. iron and sulphate) into surface waters and groundwater. As the acid water migrates, it further reacts with other minerals and dissolves a broader range of metals.

The rate of oxidation of pyrite is dependent on many factors, including the morphology of the sulphides, oxygen concentration, wetting and drying cycles, presence of bacteria and acid-consuming materials, and the geological (thermal and tectonic) history of the sulphides.

Metalliferous drainage can be formed as certain sulphide minerals oxidise, producing Acidity (see Reactions 3-6) but not directly producing acid (H^+). Acidity can therefore be present in near neutral pH waters.

Sphalerite:	$ZnS + 3/2 O_2 + H_2O$	\Leftrightarrow	$Zn^{2+} + SO_4^{2-}$	(Reaction 3)
Galena:	$PbS + 3/2 O_2 + H_2O$	\Leftrightarrow	$Pb^{2+} + SO_4^{2-}$	(Reaction 4)
Chalcocite:	$Cu_2S + 5/2 O_2 + 2 H^+$	\Leftrightarrow	$2 Cu^{2+} + SO_4^{2-} + H_2O$	(Reaction 5)
Covellite:	$CuS + 2 O_2$	\Leftrightarrow	$Cu^{2+} + SO_4^{2-}$	(Reaction 6)

1.6 Recognising the Onset of AMD

As a general guide, indications of the onset of AMD can include:

- Metal hydroxide precipitation in drainage lines (see Plate 2).
- Progressive decrease in pH (eg. ± 1.0 pH units).
- Decrease in alkalinity.
- Increase in Acidity.
- Increase in conductivity.
- High soluble metals concentrations.
- High salinity water (eg. high sulphate).

1.7 AMD Sources

Typically, sources of AMD include metal and coal mines and acid sulphate soil sites such as recent estuarine settings and mangrove swamp environments. At mine sites, AMD has the potential to occur where sulphides are exposed to oxygen and water such as open pits, underground mines, waste rock piles, tailings embankments or dams, tailings storage facilities, haul roads, ore stockpiles or heap leach pads. AMD is transported to the environment as runoff or seepage when water passes over or through the AMD generating material. AMD not only affects mine sites, but can also result from disturbance of acid sulphate soils.

2. Treatment Technologies

While AMD minimisation and control remain the focus of best practice mine site water management strategies, when AMD generation is unavoidable, appropriate treatment technologies need to be implemented. Treatment technologies are commonly categorised as either “passive” or “active”, both potentially combining physical, biological and chemical approaches. Active treatment involves regular reagent and labour inputs for continued operation, compared with passive treatment that only requires occasional maintenance. The main purpose of both types is to lower Acidity and toxic metal concentrations, raise pH and often lower sulphate concentrations and salinity.

A broad range of passive and active treatment approaches are available for dealing with AMD. General treatment mechanisms which incorporate chemical and/or physical and/or biological processes, are listed in Table 1.

Table 1. Chemical, physical and biological mechanisms for the treatment of AMD. Depending on site-specific conditions, one or a combination of these mechanisms may be suitable for AMD treatment.

AMD Treatment Mechanisms	
pH control	Oxidation
Adsorption	Electrochemical
Absorption	Sedimentation
Complexation	Flocculation-filtration-settling
Chelation	Ion Exchange
Biological Mediation	Crystallisation
Reduction	

Neutralisation (or pH control) is the most commonly used AMD treatment mechanism for both passive and active treatment systems. By increasing the pH to create alkaline conditions (eg. pH \geq 9.5), the solubility of most metals can be significantly decreased by precipitation (refer to Figure 1).

For some common soluble components of AMD, Figure 1 gives an indication of the relative solubility of bare metal ions in equilibrium with their respective metal hydroxide species (eg. aqueous Zn^{2+} in equilibrium with solid $Zn(OH)_2$) as a function of pH. Most AMD metals are “amphoteric”, that is, their solubility increases in acidic (low pH) and alkaline (high pH) conditions, and reaches a minimum at some intermediate pH value, as shown in Figure 1.

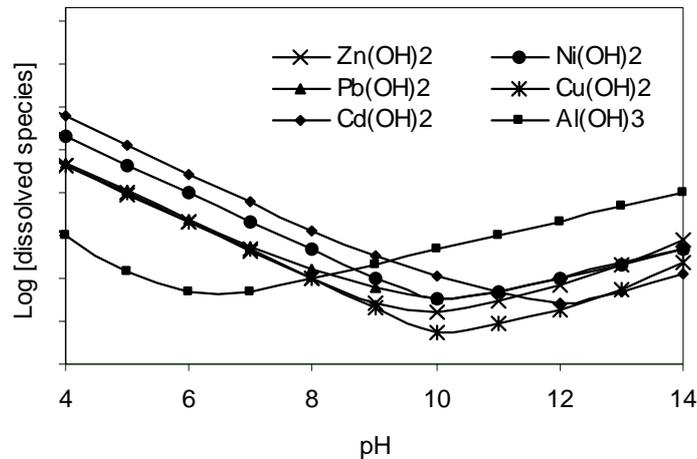
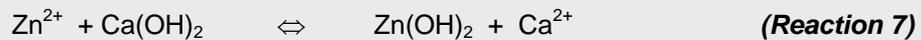


Figure 1. Affect of pH on the solubility of bare metal ions (aqueous) in equilibrium with their corresponding metal hydroxide (solid) species. Acid generation results in low pH values (eg. pH <4) which increases metal solubility. Metal concentrations, such as Cd, Ni, Zn, Cu and Pb, can be elevated at near-neutral pH. Note that the graph presents simplified trends in metal solubility (concentration is represented as "[]" on y-axis), as determined from solubility product constants, K_{sp} , of each hydroxide species. For example, the $Al(OH)_3$ graph indicates the variation in dissolved Al^{3+} concentrations with pH, assuming saturation with respect to $Al(OH)_3$. Note, the solubility of Al in equilibrium with $Al(OH)_3$ actually depends on the equilibrium of all aqueous Al species, including Al^{3+} , $Al(OH)_2^+$, $Al(OH)_2^{2+}$ and $Al(OH)_4^-$. In reality, the affect of pH on metal solubility would also depend on the type of alkalinity present (eg. hydroxide or bicarbonate alkalinity).

Table 2 lists a broad range of neutralisation materials that are currently used to introduce alkalinity and neutralise AMD. Hydrated lime ($Ca(OH)_2$) is one of the most commonly used neutralisation materials. Reaction 7 demonstrates how Acidity is neutralised by hydrated lime, using zinc as an example. The neutralisation of other metal ions or acid (H^+) could be expressed using similar reactions.



Chemical and physical properties are fundamental in choosing the most suitable and effective material for the required treatment outcomes.

For example, if precipitation of certain metals requires a pH of 10, limestone will not be effective, as it will only raise the pH to around 8 (see Table 3). Metals that can be precipitated by pH control include copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), cadmium (Cd), iron (Fe), manganese (Mn), aluminium (Al), chromium-III (Cr-III), antimony (Sb), arsenic-V (As-V), silver (Ag), selenium (Se), thallium (Th) and beryllium (Be). However, as indicated in Figure 1, the minimum solubility of most metals generally occurs at different pH values; therefore, the optimum treatment pH is site- and AMD-specific. The effect of pH control on some metals, such as cobalt (Co) and bismuth (Bi) is uncertain, while other metals are largely unaffected by



pH control alone, such as mercury (Hg), molybdenum (Mo), chromium-VI (Cr-VI) and arsenic-III (As-III). Additional treatment steps are often required if these metals are present in AMD.

While calcium- and magnesium-based carbonates such as limestone (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and magnesite (MgCO_3) may be suitable for some applications, not all mineral carbonates are capable of AMD neutralisation. For example, the neutralising capacity of mineral carbonates such as siderite (FeCO_3) and rhodochrosite (MnCO_3) is comparable to the amount of acid generated by Fe (in the case of siderite) or Mn (in the case of rhodochrosite) upon dissolution; siderite and rhodochrosite therefore cannot be used for AMD treatment. A similar problem can be encountered with ankerite ($\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$), which provides some neutralising capacity but may also generate Fe- and/or Mn-Acidity upon dissolution; the amount of Acidity produced will depend on the relative proportions of Fe and Mn in ankerite.

Table 2. Neutralisation materials that can be used for the treatment of AMD.

Neutralisation Materials	
Limestone (CaCO_3)	Sodium carbonate (Na_2CO_3)
Quicklime (CaO)	Sodium hydroxide (NaOH)
Hydrated lime ($\text{Ca}(\text{OH})_2$)	Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	Ammonia (NH_3)
Magnesite (MgCO_3)	Potassium hydroxide (KOH)
Caustic magnesia (MgO) and/or $\text{Mg}(\text{OH})_2$	Calcium peroxide (CaO_2)
Lime kiln dust (CaO , CaCO_3)	Cement kiln dust (CaO , CaCO_3)
Fly-ash (Ca, Mg, Na and K oxides and hydroxides)	Barium carbonate (BaCO_3)
Fluidised bed ash (Ca, Mg, Na and K oxides and hydroxides)	Barium hydroxide ($\text{Ba}(\text{OH})_2$)

Table 3. Chemical properties (pH and solubility) and costs associated with some AMD neutralisation materials.

Neutralisation material	Saturation pH	Solubility (mg/L) in Cold Water	AU\$ / Tonne Acid Neutralised
Limestone (CaCO_3)	8-9.4	14	15-45
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	8-9.5	10-300	15-45
Magnesite (MgCO_3)	9.5-10	60-100	
Quicklime (CaO)	12.4	1,300-1,850	130-300
Hydrated lime ($\text{Ca}(\text{OH})_2$)	12.4	1,300-1,850	150-350
Caustic magnesia (MgO)	9.5-10.8	1-50	300-600
Mg Hydroxide ($\text{Mg}(\text{OH})_2$)	9.5-10.8	1-50	400-650
Soda Ash (Na_2CO_3)	11.6	75,000	500
Caustic Soda (NaOH)	14	450,000	700-900
Ammonia (NH_3)	9.2	900,000	400-600



Passive treatment approaches are economically attractive, but have some significant limitations. They are best suited to the treatment of waters with low Acidity (<800 mg CaCO₃/L), low flow rates (<50 L/s) and therefore low Acidity Loads, where the key chemical outcome is a near neutral pH and associated low metal concentrations. With only a few exceptions, passive systems cannot handle Acidity Loads in excess of 100-150 kg of CaCO₃ per day. When specific metal reduction targets need to be achieved, as opposed to simple neutralisation, most passive treatment technologies are not suitable. When used in isolation, passive treatment systems have proven to be most successful at addressing post closure AMD issues, particularly at some coal mines. It is important that they are utilised within their chemical and physical limitations. Passive treatment systems can provide low cost solutions unless they are used for inappropriate applications, which have resulted in many being far more costly (per tonne of acid neutralised) than conventional active treatment plants.

Unlike their passive counterparts, active treatment systems can be engineered to accommodate essentially any Acidity, flow rate and daily Acidity Load. Although not limited by tight operational parameters as in the case of passive systems, the chemical flexibility of active treatment systems comes at a price. Economic considerations (ie. capital and ongoing operating costs) play a significant role in determining the viability of active treatment systems. Table 4 shows some fundamental differences between the capabilities of passive and active systems.

Table 4. Broad guidelines for determining the suitability of passive and active treatment systems based on influent water characteristics.

Treatment System	Av. Acidity Range (mg CaCO ₃ /L)	Av. Acidity Load (kg CaCO ₃ /day)	Av. Flow Rate (L/s)	Typical pH range	Max pH attainable
Passive	1–800	1–150	< 50	> 2	7.5–8.0
Active	1–10,000	1–50,000	No Limit	No Limit	14

On a plot showing AMD flow rates (in L/s) versus Acidity values (in mg CaCO₃/L), the treatment capability “fields” for a range of passive and active treatment systems is shown in Figure 2. Contours on this plot show daily Acidity Loads in tonnes of CaCO₃. The fields for most passive treatment systems lie in the boxed portion in the lower left hand corner of this plot and this area is expanded to show more detail in Figure 3.

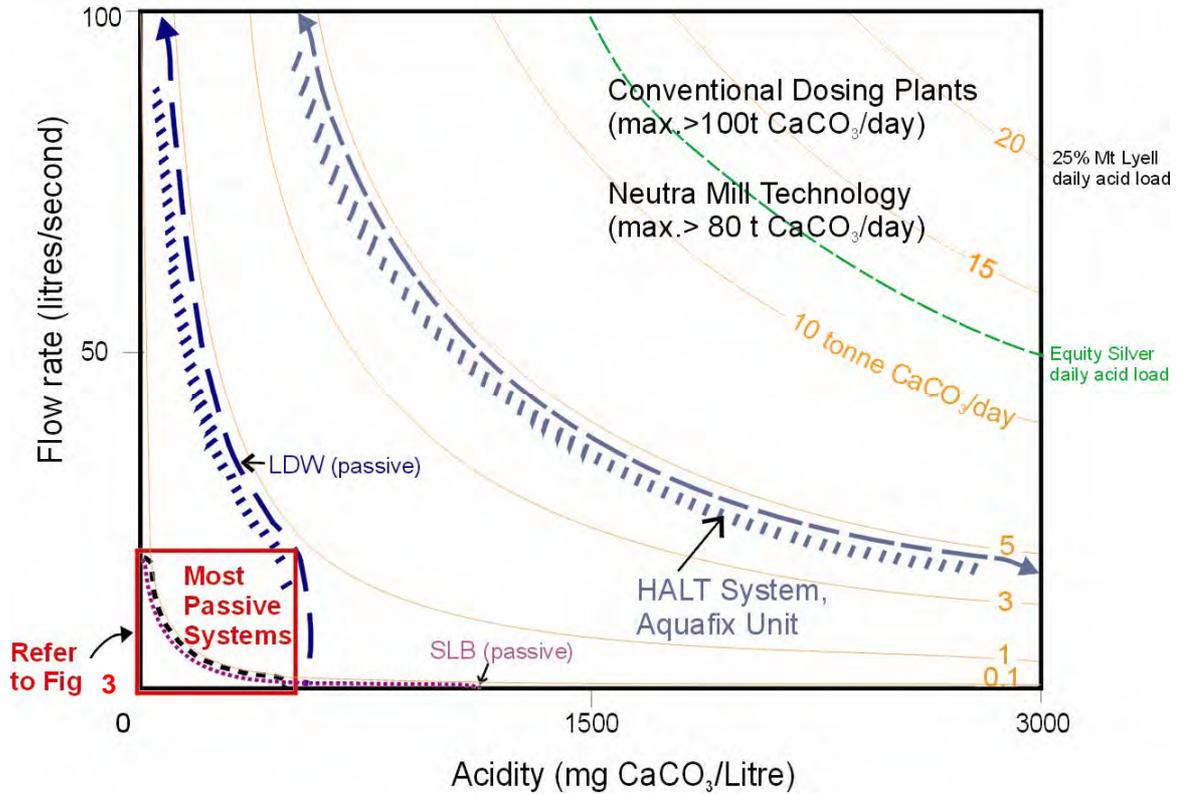


Figure 2. "Acidity Load" guidelines for selecting effective active and passive treatment systems. Contours shown are for Acidity Loads in tonne CaCO₃/day. Daily Acidity Loads associated with two well known mine sites are included for reference. The capability fields of passive treatment systems have been expanded in Figure 3. The HALT (Hydro-Active Limestone Treatment) system and Aqua-fix Unit are active treatment systems; Limestone Diversion Wells (LDW) and Slag Leach Beds (SLB) are passive treatment systems.

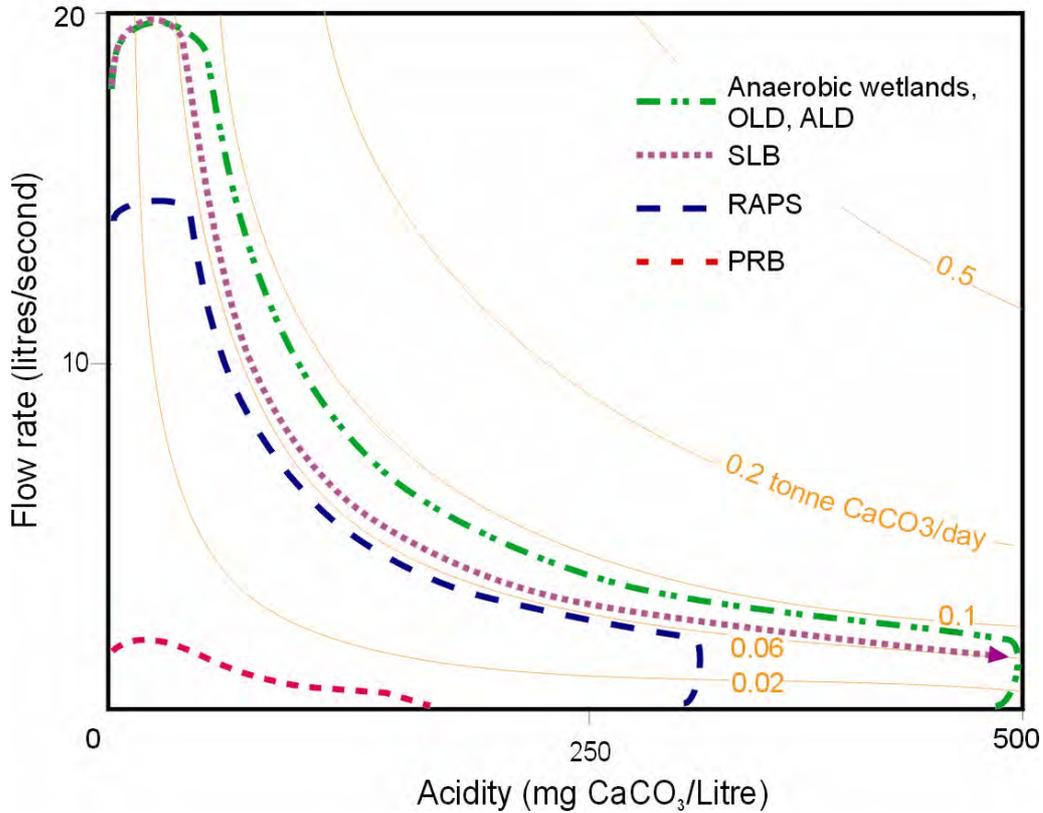


Figure 3. "Acidity Load" guidelines for selecting effective passive treatment systems. Contours shown are for Acidity Loads in tonne CaCO₃/day. The capability fields of active treatment systems are shown in Figure 2. Passive treatment systems include anaerobic wetlands, Open/Oxic Limestone Drains (OLD), Anoxic Limestone Drains (ALD), Slag Leach Beds (SLB), Reducing and Alkalinity Producing Systems (RAPS) and Permeable Reactive Barriers (PRB).

3. Passive Treatment Systems

Passive treatment systems are commonly but not exclusively aggregate-carbonate based, with or without the inclusion of organic matter. The design of passive systems must accommodate slow reaction rates and focus on minimising armouring (the coating of neutralising material with metal precipitates and/or gypsum). The scale of the systems is crucial their success, with water retention times essential in accounting for slow reaction kinetics (eg. slow limestone dissolution). Organic matter can be used to control the redox state of the system in order to minimise armouring. The life expectancy of a passive treatment system depends on the mass of limestone and/or organic matter in the system. The available porosity within the limestone and organic matter can also affect the life expectancy, as porosity determines the capacity to store treatment precipitates. Operation of a passive treatment system may become ineffective if the system gets blocked with treatment precipitates due to insufficient porosity within the limestone/organic matter layers. Passive treatment systems provide low cost solutions with low to medium capital costs (AU\$5,000-200,000) and generally very low operating costs (<AU\$1,000 / year).

Passive treatment systems cannot be regarded as walk-away solutions. However, the correct implementation of a passive system will maximise its life expectancy. At present, most passive treatment systems are used for post closure, low Acidity Load treatment scenarios, not for operating mine sites. Furthermore, as many passive treatment systems are carbonate-based, not all metals are removed from AMD waters due to maximum pH limitations (eg. Mn is not completely removed).

The armouring of limestone aggregate by precipitates and gypsum is a key problem that can greatly reduce the effectiveness of limestone-based passive treatment systems. While armouring is a problem, precipitate formation provides a clear indication that the system is working. As well as clogging flow pathways through the substrate, armouring also retards the reactivity of limestone. Armouring by iron precipitates can sometimes be partially overcome by the addition of organic matter, which maintains reducing conditions within the treatment system. Other approaches are to maximise the available surface area of the limestone and/or provide sufficient agitation within the system for the continuous abrasion of armoured surfaces.

Table 5 lists many of the passive treatment methods in use at present, including some new and emerging technologies.



Table 5. Methods for passive treatment of AMD, including new and emerging technologies.

Passive Treatment Methods	
Open/Oxic limestone drains (OLD)	Successive alkalinity producing systems (SAPS)
Anoxic limestone drains (ALD)	Permeable reactive barriers (PRB)
Limestone diversion wells (LDW)	Slag leach beds (SLB)
Pyrolusite® limestone beds	Microbial reactor systems (MRS)
Aerobic and anaerobic wetlands	Sulphide passivation compounds
Reverse alkalinity producing systems (RAPS)	Alkalinity producing covers
Vertical flow wetlands (VFW)	Gas Redox and Displacement System (GaRDS)
Alkalinity producing systems (APS)	Electrochemical covers

3.1 Oxid/Open Limestone Drains (OLD)

Oxic or Open Limestone Drains (OLD) are open channels containing coarse limestone aggregate (Ziemkiewicz and Brant, 1996). These systems make no attempt to exclude oxygen or minimise precipitate formation, and hence may have a short operational life if installed in inappropriate situations. A larger mass of limestone is used in these systems compared to Anoxic Limestone Drains (ALD; see below) to cater for their reduced efficiency due to armouring. OLD’s can be constructed (artificial) drains or they can be installed along existing drainage systems. To meet flow and Acidity Load requirements, large areas may be required for effective OLD operation.

The channel dimensions (particularly length) and slope directly affect the success of OLD’s. For example, the drain must be long enough to ensure that AMD has sufficient contact time with limestone (eg. optimally several hours) for neutralisation to occur. Where the slope exceeds 10°, water can pass through the limestone layer too quickly, preventing adequate AMD neutralisation. Where the gradient of the drain is too low, metal precipitates can accumulate around limestone particles and within void spaces. This can reduce the neutralising capacity and affect the flow characteristics of the drain.

OLD’s are designed to raise the pH of water to 6–8, introduce alkalinity acid and lower soluble metal concentrations. OLD’s are best suited to treat AMD with the characteristics shown in Table 6.

Table 6. Characteristics of influent AMD required for successful passive treatment using Open/Oxic Limestone Drains (OLDs).

Av. Acidity Range (mg CaCO₃/L)	Av. Acidity Load (kg CaCO₃/day)	Av. Flow Rate (L/s)	Oxygen Concentration	Typical pH range	Max pH attainable
< 500	< 150	< 20	Ambient	> 2	6–8

The low construction and operating costs of OLD's has made them a common treatment choice in the past. Examples of OLD's include the South Casselman River in West Virginia and at Catawissa Creek Watershed, Brandy Camp site and Tioga River Watershed in Pennsylvania (Waters et al., 2003). Although aquatic life returned to many of the affected streams, the effluent pH did not reach neutrality at any of the locations. Net alkaline effluent water was only observed to be exiting the OLD's at the Catawissa Creek Watershed; effluent water at the other sites remained net acidic. According to field results from a number of locations, it is evident that OLD's are capable of removing from solution approximately 70% of Fe, 40-50% of Al, and 10-20% of Mn (Skousen, 2002). As with all limestone-based treatment techniques, not all metals may precipitate out of solution. The dissolution of carbonates raises the pH of the water to a maximum of 7.5-8.0 in the field; only those metals that reach saturation below this pH will precipitate and be removed from solution.

OLD's are not walk-away solutions, but require ongoing maintenance to ensure maximum life and effectiveness.

3.2 Anoxic Limestone Drains (ALD)

Anoxic Limestone Drains (ALD) are layers of coarse limestone aggregate buried in carefully constructed drainage lines along gently graded slopes (Kilborn, 1999). The limestone drain is encased within a low permeability liner and capped with clay. Care is taken to avoid the possibility of covering the limestone with clays or organic matter during operation, and to ensure that negligible air can be entrained into the drain. Synthetic liners are often used to encase the aggregate filled channels to facilitate oxygen exclusion. Acidic AMD is delivered directly into the covered drains as close to the source as possible, to avoid significant oxidation. Low oxygen conditions are maintained within the drain in order to keep dissolved iron in its reduced state (ie. ferrous iron; Fe^{2+}). An elevated dissolved oxygen concentration within the influent AMD has the potential to promote the oxidation of ferrous iron to ferric iron (Fe^{3+}), which can precipitate as iron-oxide/hydroxide (eg. $\text{Fe}(\text{OH})_3$). Formation of these precipitates can result in premature system failure due to limestone armouring, which can also significantly reduce the rate of limestone dissolution. Almost all operating ALD's experience some armouring by iron precipitates. Long residence times (eg. at least 10-15 hours) are encouraged to prolong the interaction between the AMD and limestone.

The prime function of Anoxic Limestone Drains is to raise the pH of AMD to 6–8 and to optimise the addition of bicarbonate alkalinity to the water. Aerobic ponds/wetlands at the outflow end of ALD's facilitate oxidation and precipitation of iron and other metal precipitates. However, not all metals will precipitate post treatment as effluent from ALD's reaches a maximum pH of only 6–8. Further acid (H^+) will be generated upon precipitation of these metals; however, it is the intention of ALD's that sufficient excess alkalinity is produced within the drain to neutralise the additional acid that is generated when precipitation occurs in the aerobic pond/wetland.

ALD's are most effective for influent water with the characteristics shown in Table 7.



Table 7. Characteristics of influent AMD required for successful passive treatment using Anoxic Limestone Drains (ALD's).

Av. Acidity Range (mg CaCO ₃ /L)	Av. Acidity Load (kg CaCO ₃ /day)	Av. Flow Rate (L/s)	Dissolved Oxygen (mg/L)	Typical pH range	Max pH attainable
< 500	< 150	< 20	< 1	> 2	6–8

ALD's should not be used to treat AMD containing high concentrations (> 1mg/L) of Al as essentially all of the Al will precipitate as aluminium hydroxide hydrate (ie. Al(OH)₃.3H₂O) upon contact with limestone and hinder water movement through the system. In many cases, the design life of ALD systems has not been achieved due to influent AMD containing significant concentrations of Al, which results in plugging of void spaces within the drain. The design of ALD's therefore needs to incorporate sufficient porosity to ensure that plugging will not result in failure of the ALD during its design life.

Like iron-oxides, gypsum (CaSO₄.2H₂O) formation can also cause armouring of the limestone surface which retards further dissolution. The ability of ALD's to generate alkalinity can be significantly reduced and failure of the system can occur, due to various types of precipitate formation. The deployment of magnesium-rich carbonates has the potential to minimise problems associated with gypsum armouring in ALD's, but will generate drainage with a higher salinity.

ALD's are more suited to the treatment of AMD from coal mines than from metal mines because coal mines are generally associated with reduced water, in which iron precipitation is minimised. As long as the reduced state of influent AMD is maintained in the ALD, the rate of armouring of limestone with iron precipitates and associated blocking of ALD flow pathways should be minimal. Coal mines also tend to be associated with relatively low Acidity and Acidity Loads and relatively low sulphate drainage. The amount of treatment precipitates produced from coal mine AMD is therefore relatively low; this further reduces the rate of armouring of limestone with treatment precipitates and blocking of ALD flow pathways. Nevertheless, the effectiveness of ALD's can be limited if the influent AMD contains aluminium concentration in excess of 1 mg/L, due to armouring and blocking of pore spaces with amorphous Al(OH)₃.3H₂O precipitates.

Anoxic Limestone Drains provide a relatively inexpensive form of alkalinity addition. Maintenance costs for ALD's are very low, and are associated with periodic inspection of the ALD and upkeep of the vegetation cover. However, maintenance of the limestone layer can prove difficult due to the buried trench design of the system.



3.3 Limestone Diversion Wells (LDW)

Limestone Diversion Wells (LDW) provide a treatment option for sites that offer a suitable topographic fall. LDW's consist of a well (eg. an in-ground metal or concrete tank) that contains crushed limestone aggregate. Part of a fast flowing AMD stream is diverted, often via a pipeline, into the well (Milavec, 1999; Ziemkiewicz and Brant, 1996). The hydraulic force causes attritional grinding and abrasion of the limestone gravel, ensuring that armouring of the aggregate is prevented and a fine-grained limestone slurry overflows from the top of the well back into the main body of the AMD stream. In this way, partially treated water and excess particulate alkalinity is introduced back into the waterway.

LDW's are suitable for treating AMD with the characteristics shown in Table 8.

Table 8. Characteristics of influent AMD required for successful passive treatment using Limestone Diversion Wells (LDW's).

Av. Acidity Range (mg CaCO ₃ /L)	Av. Acidity Load (kg CaCO ₃ /day)	Av. Flow Rate (L/s)	Oxygen Concentration	Typical pH range	Max pH attainable
< 500	1–1,000	< 1000	Ambient	> 2	6–8

The successful use of a LDW requires approximately a 10 metre elevation change or more between the locations of the diversion and the well. If the elevation change is less than 10 metres, there may be insufficient water velocity to turbulently mix and abrade the limestone particles. Furthermore, insufficient alkalinity may be produced and metal precipitates could block the well, subsequently preventing its operation. During periods of higher than normal flow, the rate of alkalinity generation within the LDW may not be adequate to suitably neutralise the AMD-affected stream. There have been both successes and failures regarding the use of LDW's in the field (Waters et al., 2003).

Significant maintenance is required for the operation of a LDW that discourages the remote operation of these systems. Limestone can only be added to the well in small amounts so that frequent refilling with clean limestone is required to assure continued treatment. Nevertheless, limestone is inexpensive and readily available. Hopper feed systems can be installed to allow limestone to be automatically fed into the LDW as the reagent is consumed. Hopper feed systems do not eliminate the requirement for regular refilling of the LDW, but they reduce the frequency of refilling by increasing the reagent storage capacity of the system. Maintenance of LDW's also involves the regular removal of leaves and other debris from the well to avoid blocking.

As the metal precipitates are not captured within the LDW, sludge tends to accumulate within the waterway and may require removal (eg. by construction of a settling pond).

Key benefits of LDW's include the minimisation of limestone armouring due to the vigorous mixing of AMD inflow and limestone aggregate, and greater efficiency of limestone use compared to OLD's and ALD's. However, reagent use may only be 50% efficient, and LDW's are not walk-away solutions.



3.4 Pyrolusite® Limestone Beds

Pyrolusite® Limestone Beds consist of limestone beds or channels inoculated with aerobic micro-organisms (generally algae) and are primarily constructed to treat AMD containing high concentrations of manganese. The aerobic micro-organisms produce oxygen (O₂) which catalyses the hydrolysis of Mn²⁺ to the insoluble MnO₂ (pyrolusite). The reaction generates 4 moles of H⁺ (refer to Reaction 8), which is neutralised by the limestone. Pyrolusite® Limestone Beds are also suitable for the removal of iron. The beds are usually preceded by an aerobic wetland to provide nutrients for the micro-organisms and to provide some initial treatment (ie. oxidation).



Pyrolusite® Limestone Beds are best suited where the majority of the Acidity is related to soluble manganese concentrations (Milavec, 1999). AMD with the characteristics shown in Table 9 is generally suitable for treatment with Pyrolusite® Limestone Beds.

Influent AMD should not contain high concentrations of iron as build-up of iron-oxide precipitates, particularly at the pyrolusite bed entrance, can occur. Ongoing maintenance of a Pyrolusite® Limestone Beds is necessary as the organic substrate must be periodically replaced and precipitates removed by routine flushing.

Table 9. Characteristics of influent AMD required for successful passive treatment using Pyrolusite® Limestone Beds.

Av. Acidity Range (mg CaCO ₃ /L)	Av. Acidity Load (kg CaCO ₃ /day)	Flow Rate	Oxygen Concentration	Typical pH range	Max pH attainable
< 500	1–500	Permit maximum residence time (eg. > several hours)	Ambient	3–5	6–8

3.5 Wetlands

Natural wetlands are complex ecosystems comprising water-saturated soil and sediments with supporting vegetation that have the capacity to naturally improve water quality via a range of physical, chemical, microbial and plant-mediated processes. These include oxidation, reduction, precipitation, sedimentation, filtration, adsorption, complexation, chelation, active plant uptake of metals and microbial conversion / immobilisation mechanisms (Kilborn, 1999; Milavec, 2002; Ziemkiewicz et al., 2002). Key factors that need to be considered when determining the type, size and cost of an appropriate wetland system include:

1. The influent Acidity Loads, pH and redox state.
2. Water flow rates and retention times.
3. The area available for a wetland.

There are two broad types of constructed wetland, aerobic and anaerobic.

Aerobic Wetlands

Aerobic wetlands are essentially shallow ponds that lower suspended solids and provide a substrate and increased water retention times (due to reduced flow rates) for the reaction between influent alkalinity and Acidity that is generated from AMD via metal oxidation and precipitation within the wetland.

Aerobic wetlands contain vegetation planted in relatively impermeable sediments (eg. clay). Refer to Plate 3. Aerobic wetlands differ to all other passive treatment techniques in that they do not neutralise AMD. They must receive net-alkaline water, often diverted from a pre-treatment passive system, and solely provide residence time and aeration to allow certain metals whose solubility is dependant on the redox state of the water (eg. iron, manganese, chromium, arsenic) to precipitate. Precipitates are retained on plant surfaces, in the wetland, or downstream.

Successful performance of aerobic wetlands requires the influent AMD to have the characteristics shown in Table 10. Moreover, dissolved oxygen concentrations need to have reached saturation with respect to the atmosphere early within the residence time of the water in the wetland.

Table 10. Characteristics of influent AMD required for successful passive treatment using Aerobic Wetlands.

Av. Acidity Range (mg CaCO₃/L)	Av. Acidity Load (kg CaCO₃/300m² of wetland)	Flow Rate	Oxygen Concentration	Typical pH range	Max pH attainable
< 500	≤ 1 (Kilborn, 1999)	Permit maximum residence time (eg. 1-5 days)	Ambient	> 6	n/a

The size of the wetland is an important factor in the success of AMD treatment. Design must take into account total Acidity Loads and water flow rates. Often wetlands are undersized leading to inadequate retention times and poor effluent water quality.

Although aerobic wetlands have proven effective in many situations for the removal of Fe (60–95%) from solution, they generally fail to adequately remove Mn. Commonly, less than 10% of Mn is precipitated from solution in aerobic wetlands due to insufficient alkalinity levels, and an inability of the system to reach pH levels greater than 8. Management issues arise regarding the removal and disposal of the metal precipitates deposited within or downstream of the wetland.

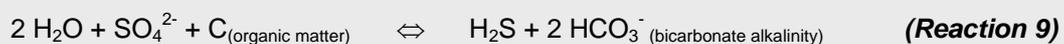


Plate 3. Aerobic wetland for the passive treatment of mine waters.

Anaerobic Wetlands

Anaerobic wetlands are water retention ponds comprising a substrate of organic matter and/or limestone aggregate. Anaerobic wetlands encourage AMD passage through organic-rich material that strips oxygen from the water, resulting in anaerobic conditions. The wetlands may contain a layer of limestone beneath the organic substrate, or the limestone may be mixed among the organic matter.

Alkalinity in the wetlands can be generated by sulphate reducing bacterial (SRB) activity, which use the organic matter as a carbon source and sulphate as an electron acceptor for growth. In the bacterial conversion of sulphate to hydrogen sulphide, bicarbonate alkalinity is produced (Reaction 9).



Alkalinity can also be generated from the dissolution of limestone (if present) upon contact with AMD.

Metal concentrations can be decreased via precipitation of metal sulphides in the reduced (anaerobic) organic layer of the wetland. In addition, some metals can be removed as carbonate precipitates, due to the presence of bicarbonate alkalinity provided by limestone dissolution and/or SRB activity.

Anaerobic wetlands are best suited to treat AMD with the characteristics shown in Table 11. While ambient oxygen concentrations are acceptable at the surface, highly reducing conditions at depth favour extended life expectancies and improved performance of anaerobic wetlands.

Insufficient wetland area and excess Acidity Loads have been responsible for the reduced lifetime of many anaerobic wetland systems. High influent Acidity Loads can result in the excessive generation of treatment precipitates, leading to armouring of limestone particles, exhaustion of sorption sites on organic material and/or blocking of pore spaces within the limestone and organic matter layers.

The life expectancy of anaerobic wetlands is generally limited by either (i) the mass of limestone or organic matter in the wetland, or (ii) the available porosity within the limestone or organic matter. Porosity determines the capacity to store treatment precipitates, which in turn affects water retention times (and therefore treatment efficiency) of the wetland.

The long term maintenance requirements of anaerobic wetlands can be minimised by encouraging the establishment of vegetation around the wetland. Deposition of plant litter into the wetland and progressive decomposition of this material can provide a continuous supply of organic inputs to the wetland.

Alternatively, artificial inputs of organic matter can be used as a successful strategy to temporarily renew the adsorption capacity of organic matter in anaerobic wetlands (Eger and Melchert, 1992).

Ongoing maintenance of anaerobic wetlands may also involve routine nutrient addition for bacterial growth, or replacement of limestone aggregate.

Table 11. Characteristics of influent AMD required for successful passive treatment using Anaerobic Wetlands.

Av. Acidity Range (mg CaCO₃/L)	Av. Acidity Load (kg CaCO₃/200- 500m²/day)	Flow Rate	Oxygen Concentration	Typical pH range	Max pH attainable
< 500	1 (Kilborn, 1999)	Permit maximum residence time (eg. 1–5 days)	Ambient near surface	> 2.5	6–8
			< 1 mg/L subsurface		

3.6 Reducing and Alkalinity Producing Systems (RAPS)

A range of approaches, collectively termed Reducing and Alkalinity Producing Systems (RAPS), have been devised to treat low Acidity, low flow, low Acidity Load, relatively reduced AMD flows. These include Alkalinity Producing Systems (APS), Vertical Flow Wetlands (VFW), Reverse Alkalinity Producing Systems and Successive Alkalinity Producing Systems (SAPS) (see Figure 4). While the precise names and construction details of these systems vary from place to place, all of these approaches have a number of factors in common (Milavec, 2002; Demchal et al., 1996).

Reducing and Alkalinity Producing Systems:

1. Utilise mixtures of limestone and organic matter and thereby represent combined inorganic and organic approaches to AMD treatment.
2. Rely on alkalinity generation via limestone dissolution and sulphate reducing bacterial (SRB) activity.
3. Enhance reducing conditions (to enable sulphide precipitation and to minimise untimely iron/manganese oxidation and precipitation/armouring).
4. Provide sites for metal adsorption (ie. on the organic matter).
5. Raise the pH of the water to near neutral conditions.

The successful performance of these systems requires the influent AMD to have the characteristics shown in Table 12.

Table 12. Characteristics of influent AMD required for successful passive treatment using Reducing and Alkalinity Producing Systems (RAPS).

Av. Acidity Range (mg CaCO₃/L)	Av. Acidity Load (kg CaCO₃/day)	Av. Flow Rate (L/s)	Dissolved Oxygen (mg/L)	Typical pH range	Max pH attainable
< 300	< 100	< 15	< 1-3	> 2.5	6–8

The type of RAPS selected for AMD treatment is generally dependent on site-specific conditions such as topography, available surface area for the treatment system, soils and geology, groundwater flows, etc., as well as the availability of resources for setting up and maintaining the treatment system. As a result, RAPS have been implemented in various forms (eg. APS, SAPS, VFW, etc.), ranging from fully engineered constructions to relatively unmodified natural systems.

Figure 4 shows a schematic cross section of a RAPS. Although discussed separately (above), anaerobic wetlands are also a type of RAPS.

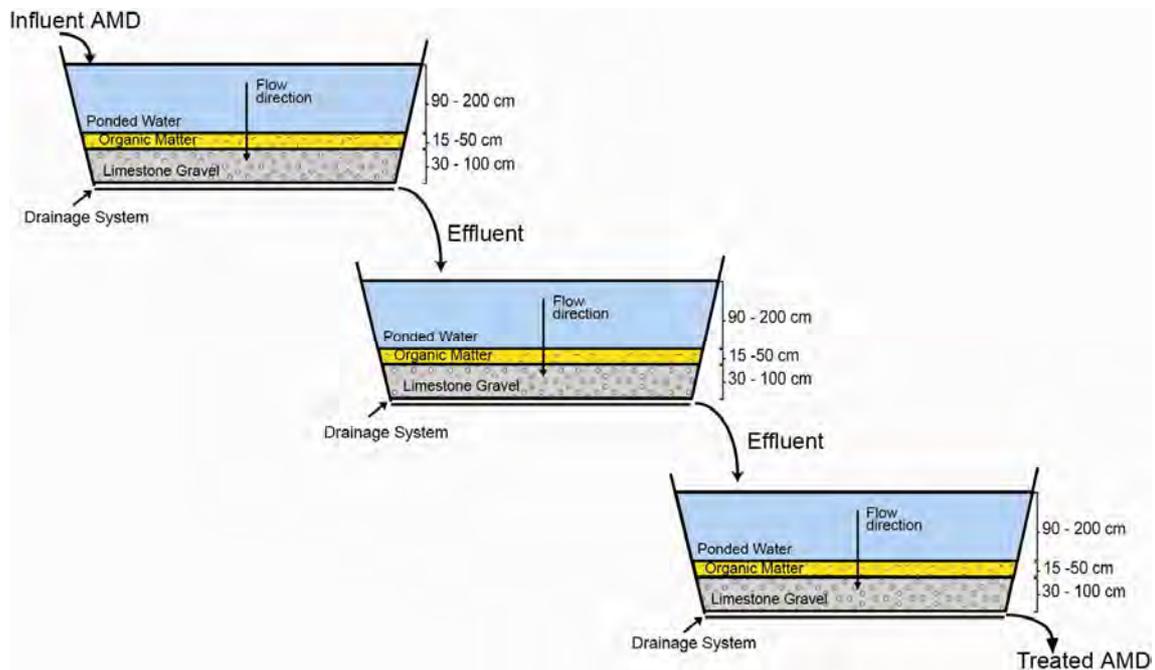


Figure 4. Typical layout of a Reducing and Alkalinity Producing System (RAPS), which utilises organic matter and limestone for the passive treatment of AMD. The system shown in this diagram is also commonly referred to as a "Successive Alkalinity Producing System".

RAPS are not walk-away solutions. Compared to other passive treatment systems, RAPS have a high capital cost and are subject to limitations associated with pore clogging by gypsum and metal precipitates. Permeability can be lowered by progressive compaction of the substrate, and high maintenance (eg. flushing) is required if aluminium precipitation cannot be prevented.

3.7 Permeable Reactive Barriers (PRB)

Permeable reactive barriers are buried layers of reactive material (eg. organic matter / limestone, zero valent iron) that are designed to intercept groundwater plumes of AMD to assist with *in-situ* remediation (see Figures 3 and 5). Organic material can promote bacterially mediated sulphate reduction which results in the reaction of aqueous hydrogen sulphide (H_2S) and hydrogen bisulphide (HS^-) with dissolved metals in the AMD to form sulphide precipitates with metals such as As, Cd, Cu, Fe, Ni, Pb, and Zn. Organic matter is consumed by the bacteria; the void spaces are progressively filled by the metal sulphide precipitates. The generation of alkalinity during microbial digestion of organic matter consumes Acidity (Reaction 9) and further enhances metal precipitation in the permeable barrier.

Two types of PRB's that are suitable for AMD treatment are Organic Rich Barriers (ORB) and an emerging AMD technology, Zero Valent Iron (ZVI) barriers (Smyth et al., 2003). ORB barrier systems can be suitable for treatment of AMD with the properties shown in Table 13.

Table 13. Characteristics of influent AMD required for successful passive treatment using organic rich Permeable Reactive Barriers (PRB).

Av. Acidity Range (mg CaCO ₃ /L)	Av. Acidity Load (tonne CaCO ₃ /year)	Av. Flow Rate (L/s)	Oxygen Concentration	Typical pH range	Max pH attainable
< 500	1-5	< 1	Relatively reduced	> 3	> 6.5

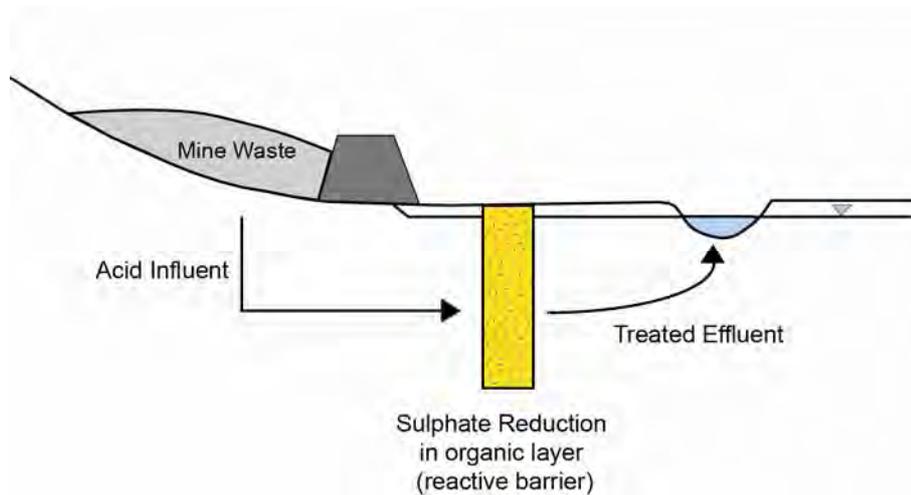


Figure 5. Permeable Reactive Barriers may be used to intercept and treat acidic groundwater in-situ.

For PRB's to effectively treat AMD, water entering the barrier must have a low oxygen concentration when it contacts the reactive barrier. Successful neutralisation of AMD involves the conversion of Fe³⁺ to Fe²⁺ upon contact with the barrier and precipitation of iron sulphides (and other metal sulphides) within the barrier. The key factors which may limit the lifetime of PRB's are the mass of available reactive material and the available volume of pore spaces (and permeability) of the barrier. Metal precipitation and substrate compaction can result in a decrease in porosity and permeability of the barrier. Permeable Reactive Barriers are ideally suited to cold climates as low soil temperatures (<5°C) inhibit bacterial activity.

3.8 Slag Leach Beds

Slag Leach Beds (SLB) are channels or barriers (eg. check dams) containing fine-coarse slag aggregate. SLB's can be constructed (artificial) or they can be implemented along existing drainage lines. A range of slag materials are available as by-products of the steel manufacturing process. The composition of the slag depends on the type of steel manufacturing process; blast furnace slag is generally the most suitable material for SLB's.

SLB's are similar in concept to Oxidic Limestone Drains, but utilise slag materials in place of limestone aggregate. Blast furnace slags are calcium silicate rich glasses with substantial inherent neutralisation capacity. The glasses are unstable in the presence of water and release alkalinity upon decomposition.

Trace metal concentrations in the slag typically include aluminium, magnesium, iron, titanium, manganese and silica. The effectiveness of water treatment may be adversely affected by the dissolution of trace metals from the slag material. Nevertheless, blast furnace slag can raise the pH of water to above 10, promoting the precipitation of most metals.

SLB's are best suited to treat AMD with the properties shown in Table 14.

Table 14. Characteristics of influent AMD required for successful passive treatment using Slag Leach Beds (SLB's).

Av. Acidity Range (mg CaCO ₃ /L)	Av. Acidity Load (tonne CaCO ₃ /year)	Av. Flow Rate (L/s)	Oxygen Concentration	Typical pH range	Max pH attainable
< 1000	1-2	< 20	Ambient	> 1.5	>10

Although only 60 wt% of the slag volume dissolves during reaction, it still provides a similar neutralising capacity to limestone. However, the cost-efficient implementation of SLB's requires that a slag supply be located in close proximity to the treatment site, as material transport will increase the overall costs substantially. Due to the limited availability of slag and the resulting high cost of transport, the widespread use of SLB's is hindered.

3.9 Sulphide Passivation / Micro-Encapsulation Technologies

Sulphide passivation or micro-encapsulation technologies have been proposed for the prevention or minimisation of AMD from pit wall faces. These technologies are designed to prevent air and water reacting with individual sulphide crystals by chemical encapsulation.

Chemical compounds with the potential to coat the surface of exposed pyrite crystals, could potentially be used to prevent or control pyrite oxidation. Compounds that have been trialled include furfuryl alcohol resin sealant ((C₄H₃O)CH₂OH), potassium permanganate (KMnO₄), Ecobond™ (phosphate-based compound) and magnesium oxide (Mg(OH)₂).

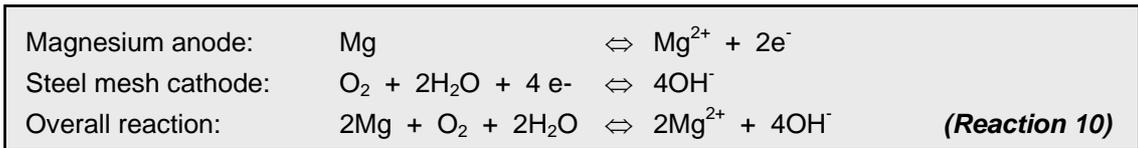


Sulphide passivation / micro-encapsulation technologies are based on the assumption that the majority of AMD generation within mining pits only occurs at the pit face; therefore these technologies do not take into account AMD formation associated with exposed (unsaturated) pit wall rock within the cone of depression surrounding a pit. Limited testing of sulphide passivation / micro-encapsulation technologies has been conducted, and preliminary test results are not encouraging.

The micro-scale approach to AMD prevention is different to methods that aim to passivate preferential flow pathways, such as alkalinity producing covers (see Section 3.11).

3.10 Electrochemical Covers

Electrochemical cover technology involves the construction of a conductive steel mesh cathode and magnesium metal anode to prevent oxygen migration through the surface of tailings material, thereby preventing AMD production. The magnesium anode can be placed at the top of the tailings material, or within a compacted soil cover, and provides electrons that migrate down to the cathode below. Oxygen is consumed at the steel mesh cathode and generates hydroxide alkalinity according to Reaction 10. Refer to Figure 6.



The steel mesh cathode approach can be applied where the sulphide content of tailings material is too low to maintain a current. However, highly sulphidic material may be conductive enough to be used as a cathode instead of steel mesh (Enpar Technologies, 2002).

Limitations of electrochemical covers include the capital and ongoing costs of anodes and cathodes. As magnesium metal is consumed during the process, the anode requires routine replacement. Electrochemical cover technology is a relatively new technique that is still under development, and there is currently no information available on large scale applications of this method.

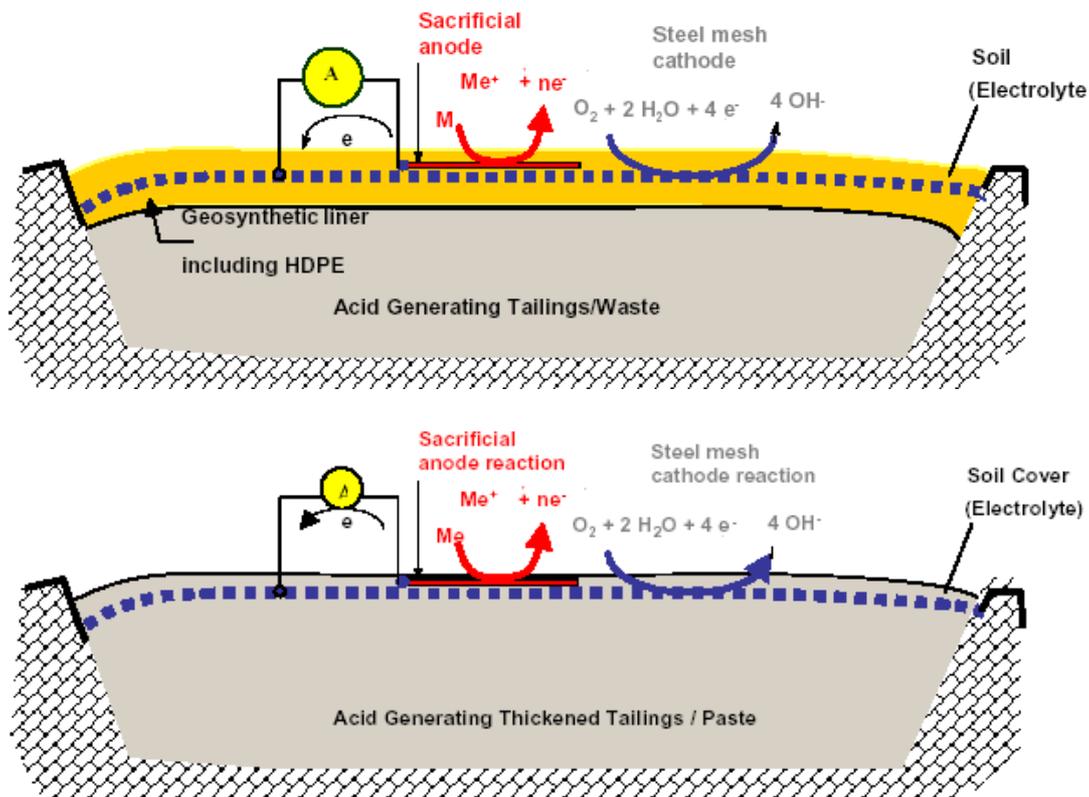


Figure 6. Top: Schematic of an electrochemical protective layer for a soil cover (top). Bottom: Schematic of an electrochemical protective layer for surface tailings and paste tailings disposal. Both diagrams have been taken from Shelp et al. (2005).

3.11 Alkalinity Producing Covers

Attempts to lower the Acidity Load discharging from waste rock piles commenced with the intimate blending of mineral carbonates with acid generating waste rock. The recognition that rapid armoring of carbonates rendered this approach largely ineffective lead to the deployment of carbonates in covers, above acidic materials. The low solubility and slow dissolution rate of all carbonates in near neutral rain water produced disappointing results from this technique, except at one site. At the Freeport mine in Indonesia, substantial improvements in the quality of drainage are being recorded from trial waste rock piles with a 2 metre limestone cap (Miller et al., 2003). Much of the success of this approach at the Freeport mine has been attributed to the 3-5 metres of annual rainfall and thick limestone cover. The mechanism responsible for the improvement in water quality is thought to be the lining of preferential flow pathways with neutralisation precipitates, generated as alkalinity is introduced to the waste via slow limestone dissolution.

While the passivation of preferential pathways would appear to be a desirable objective in waste rock piles, few sites can provide 2 metre thick limestone covers, or generate up to 5 metres of rain for limestone dissolution.



To overcome these technical, economic and climatic limitations, new magnesium-based alkaline materials with superior solubility and dissolution rate characteristics to limestone have been developed. These products should provide all mine sites with the ability to cost effectively passivate preferential flow pathways in waste rock piles. These materials will permit the controlled release of alkalinity to infiltrating rainwater over a wide range of climatic conditions. The new materials are based on calcium-enriched caustic magnesia (MgO) with controlled calcination grades and grain sizes to maximise both solubility and dissolution kinetics. Alkalinity concentrations of up to 510 mg/L CaCO₃ equivalent in pure water can be achieved with the new materials (c.f. only 10-15 mg/L for limestone), with a typical saturation pH of 9.0-9.5 (c.f. only 8.0-8.5 for limestone) (Taylor et al., 2006).

Compared to limestone, it is envisaged that relatively small amounts of these new magnesium-based materials can be deployed within existing and new cover systems to cost effectively and rapidly minimise short, medium and long term AMD discharges.

3.12 Gas Redox and Displacement System (GaRDS)

A passive treatment technique for dealing with AMD from underground mines has been jointly developed by Earth Systems and the Australian Nuclear Science and Technology Organisation (ANSTO), but has been partially tested at an abandoned mine site in Zeehan, Tasmania. The Gas Redox and Displacement System (GaRDS) approach is designed to provide an atmosphere within underground workings where metal sulphides remain stable.

GaRDS retards sulphide oxidation by displacing oxygen from underground workings (Taylor and Waring, 2001). The air is displaced from mine voids with a gas mixture comprising carbon dioxide (CO₂) and methane (CH₄), which can be generated in an external anaerobic bioreactor, or via coal-bed methane. In an anaerobic bioreactor (Plate 4), CO₂ and CH₄ are produced from the anaerobic decomposition of organic matter (eg. compost, woodchips, manure and/or hay). As the biogas (CO₂ and CH₄) concentrations build up in the anaerobic bioreactor, the gases passively migrate via a pipeline into the underground mine workings. Both CO₂ and CH₄ physically displace O₂ and progressively increase in concentration within the mine workings (up to ~50% CO₂ and ~50% CH₄, with trace concentrations of other gases) as long as they are produced at a sufficient rate to overcome the oxygen inflow rate. CH₄ also has the benefit of reacting with O₂ to produce additional CO₂, and is therefore capable of both physical displacement and chemical consumption of oxygen. To facilitate biogas build-up and discourage oxygen inflows to the mine workings, a low permeability barrier(s) is required at the mine opening(s) to prevent exposure to atmospheric conditions (Plate 5). As shown in Plate 5, water is still allowed to drain from the mine via S-bend pipeline which is designed to prevent gas transfer into the workings.

Figure 7 is an Eh-pH plot of the Fe-S-C-O-H system at 25°C, which is a good model for the GaRDS environment. The plot highlights that sulphide minerals such as pyrite will remain stable along the CO₂(gas)-CH₄(gas) join. As long as redox conditions within the mine workings are controlled by the anaerobic gas mixture, no AMD can be generated.



The GaRDS approach is expected to be useful where partial or complete flooding of underground workings is not feasible, or where pressure bulkheads on underground workings are undesirable. At present, no other passive treatment options are available for underground mines.

GaRDS may not be appropriate at sites where there is extensive collapsed ground (eg. around some coal mines) due to the presence of high permeability pathways which may prevent the accumulation of biogas within the mine workings. Similarly, GaRDS may be inappropriate where the cost of providing relatively low permeability gas barriers is prohibitive (eg. multiple connected workings in historical mining districts with adits, shafts, glory holes, pits, etc).



Plates 4-5. Gas Redox and Displacement System (GaRDS) for prevention of AMD formation in an underground mine. Left: Bioreactor used to generate CO₂ and CH₄ gases, which displace oxygen from the mine. Right: Installation of low permeability wall and drainage system at the main adit opening.

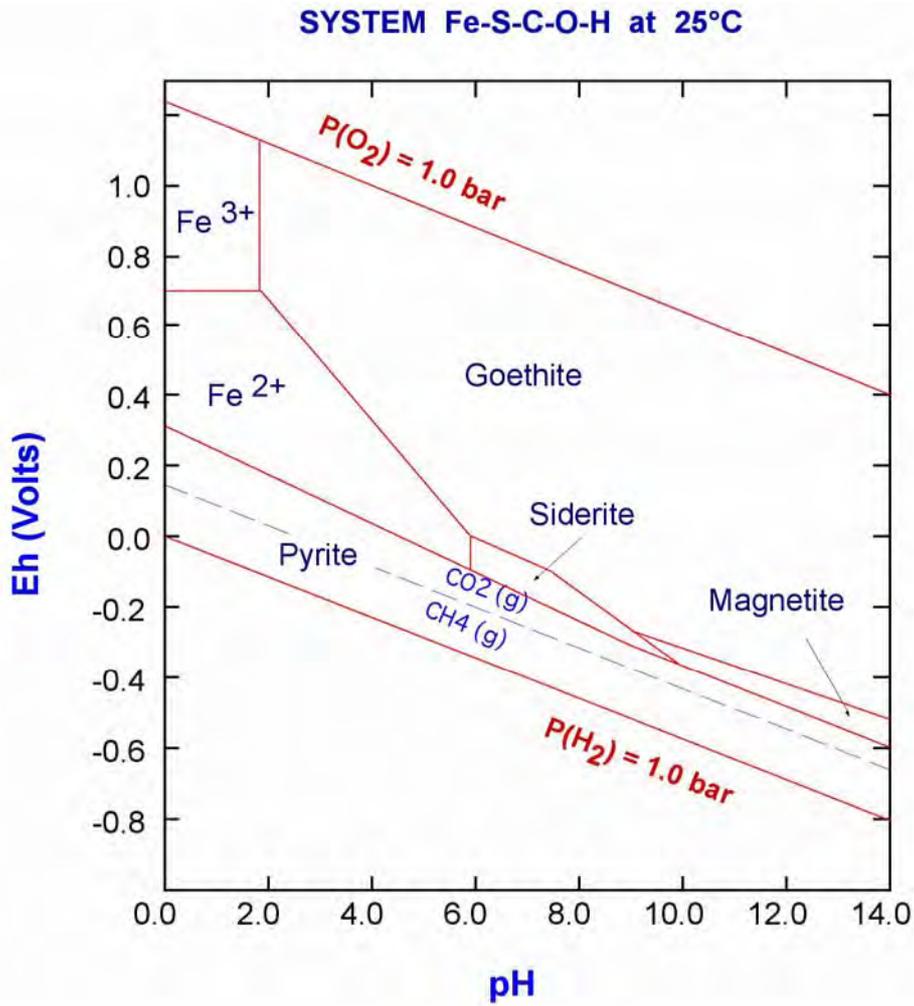


Figure 7. An Eh-pH diagram for the Fe-S-C-O-H system at 25°C. $\log a_{\text{Fe}^{2+}} = -4.0$ and $\log a_{\text{SO}_4^{2-}} = -3.0$. The $\text{CO}_2(\text{g})$ - $\text{CH}_4(\text{g})$ boundary and the siderite field are based on an atmosphere comprising approximately 0.5 bars CO_2 and 0.5 bars CH_4 partial pressure.

4. Active Treatment

Active treatment of AMD involves routine reagent addition and regular maintenance. Unlike their passive counterparts, active systems are used for both operational mine sites and occasionally post closure scenarios. Although effective, active treatment systems generally incur high capital (>AU\$100,000) and operational (>AU\$100,000 / year) costs. Sizing of the systems is crucial to account for seasonal variation in Acidity Loads, ensuring AMD is treated fully prior to discharge.

Active treatment approaches fall into two main categories: (i) fixed plant and (ii) *in-situ*. The first category comprises conventional active treatment plants that are fixed in location and typically require pumping of AMD to the plant, reagent addition and mixing in one or more reactor tanks, collection/disposal of treatment sludge, and discharge of treated water. *In-situ* active treatment approaches use portable land-based or water-based systems to conduct treatment within or adjacent to an affected water body (eg. pit lake) or stream.

Infrastructure requirements associated with *in-situ* active treatment are relatively minor and treatment costs (capital and operating) are generally considerably lower than for fixed plants.

The cost of diverting AMD to a fixed plant is a key factor in determining whether *in-situ* treatment is preferable to using a fixed plant. *In-situ* treatment becomes a viable alternative to a fixed plant when the cost of diverting the AMD to a fixed plant exceeds the cost of taking a smaller, portable plant to the water.

Of the broad range of treatment approaches available for dealing with AMD (Table 1), active systems (*in-situ* and fixed plant) utilise the following key chemical and physical processes:

- pH control or precipitation.
- Electrochemical concentration.
- Biological mediation / redox control (sulphate reduction).
- Ion exchange / absorption or adsorption / flocculation and filtration.
- Crystallisation.

Control of pH with inorganic alkaline amendments is by far the most common and cost-effective form of general purpose active AMD treatment. A large variety of natural, manufactured or by-product alkaline reagents is available, with their use dictated by availability, cost and performance. Alkaline reagents treat AMD by increasing the pH and decreasing metal concentrations by promoting the precipitation of heavy metals, often as hydroxide complexes (refer to Figure 1).

The successful implementation and the sustainability of pH control/precipitation treatment systems requires the selection of a reagent appropriate for the treatment task and an efficient mixing and dispensing mechanism. Conventional alkaline reagents used for active treatment of AMD include:

- Hydrated lime (Ca(OH)₂).
- Quicklime (CaO).
- Caustic soda (NaOH).
- Soda ash (Na₂CO₃).
- Ammonia (NH₃).
- Magnesium oxide / hydroxide (MgO / Mg(OH)₂).
- Mineral carbonates (eg. limestone, dolomite, magnesite and witherite).

Less common alkaline reagents include Lime Kiln Dust (LKD) and Cement Kiln Dust (CKD), fly-ash, fluidised bed combustion ash, calcium peroxide, potassium hydroxide and seawater neutralised red mud (from bauxite processing).

Table 15 details a number of important issues associated with the use of chemical neutralisation for both *in-situ* and fixed plant active treatment that should be taken into consideration when choosing an appropriate treatment system.

Table 15. Chemical neutralisation issues for in-situ and fixed plant active treatment of AMD.*

Issue	Comment
Reagent availability and cost	Important in determining the most suitable reagent for the treatment system.
Reagent purity	Critical to system operation as impurities can alter chemical processes / conditions, leading to ineffective or incomplete treatment. Reagent purity can determine cost effectiveness of the reagent.
Reagent solubility and dissolution rate	Solubility and dissolution characteristics must be suited to site-specific AMD generation rates and resulting Acidity Loads.
Reagent supply, storage, delivery and dispensing techniques (materials handling)	Availability and cost of treatment materials and equipment can influence selection of AMD treatment systems.
Occupational health and safety	Some reagents (eg. quicklime, CaO) have associated health and safety risks. Careful handling may be required to avoid burns, dust production, etc.
Adequate mixing / reactions times / aeration techniques	Effective treatment requires sufficient aeration, mixing and reaction times to enable complete neutralisation of AMD. Aeration may be needed to create appropriate redox conditions for treatment (eg. oxidised conditions are required to convert "latent" Acidity into acid, prior to the neutralisation stage). Armouring can be minimised by continuous mixing and abrasion of neutralisation reagents.

Issue	Comment
Efficiency of reagent use	Reagent dosing needs to be carefully controlled to avoid saturation with respect to the neutralising reagent, and thus maximise reagent use efficiency.
Properties of reagent in water	Reagent impurities may adversely affect the treatment process (eg. by affecting redox conditions or introducing new contaminants to the AMD).
Sludge	The cost and logistics of sludge management are affected by the mass and volume of sludge produced, the sludge density, and the chemical composition and stability of treatment precipitates in the sludge.
Power source	Availability of a suitable power supply may influence selection of AMD treatment system, particularly for portable treatment systems.
End use of water	Treatment objectives depend on the desired end use of treated water. Objectives may be related to off-site discharge, recycling of water with the site, or infrastructure protection.

* Neutralisation requirements and costs for treating AMD can be estimated using the ABATES shareware tool, which takes into account different reagent types, costs, purity of reagent, efficiency of reagent use.

The management of treatment sludge is a particularly important consideration, as disposal costs can occasionally be as high as treatment costs. Potential issues associated with sludge generation from active AMD treatment include:

- Possible re-mobilisation of unstable precipitates contained in the treatment sludge, necessitating re-treatment of the water.
- Possible delay in sludge formation due to incomplete oxidation at the treatment site, resulting in off-site (downstream) deposition of sludge.
- Downstream transport and deposition of sludge formed from in-situ treatment of AMD-affected channels or streams.

4.1 Fixed Plants for AMD Treatment

A wide variety of general purpose and proprietary, fixed plant, dry powder and liquid mixing and dosing systems are available for the treatment of AMD. The principal benefit of conventional neutralisation plants is that they can be engineered to handle any Acidity Load or unexpected eventuality and achieve most water quality targets (see Figure 2). Although the capital and operating costs of such systems are relatively high, they employ well-established technology and are highly reliable. A key limitation of fixed plant systems is the need to deliver affected water to the plant, regardless of the number of discrete AMD sources. Significant additional costs are incurred when the AMD source is some distance from the plant. These costs are associated with piping and pumps (and electrical power) required to transport AMD flows over long distances, especially in mountainous terrain. Furthermore, fixed plants offer little flexibility.

4.1.1 **Low Density Sludge Plants (pH control / precipitation)**

Low Density Sludge (LDS) plants are the most common fixed plants for AMD neutralisation worldwide and typically involve three main treatment stages (refer to process flow sheet in Figure 8):

- Reagent mixing and dosing stage. A solid neutralisation reagent is mixed with water in a tank to produce a slurry. The reagent slurry is then dosed into a reactor containing influent AMD.
- Reaction stage. The solution is mixed using mechanical stirrers and aerated if necessary to oxidise any reduced metals (eg. convert Fe^{2+} to Fe^{3+}). Mixing and/or aeration is continued as the solution flows through one or more reactors. The volume of reactor(s) needs to provide sufficient water retention capacity to allow complete oxidation and neutralisation.
- Flocculation and clarification stage. Neutralised water from the reaction stage is transferred to a clarifier/thickener tank (Plate 8). The flow velocity is significantly reduced in the clarifier, and a flocculant may be added during this stage, to facilitate sludge settling. Sludge from the clarifier base is removed and generally disposed on site (Plate 9), while supernatant water is discharged from the plant.



Plates 8-9. Above: Low Density Sludge (LDS) plant incorporating thickener tank (background), series of reactor tanks (left of photo), and lime slurry mixing and dosing system (foreground). Right: Large sludge disposal areas are required for dewatering of treatment precipitates discharged from LDS plants.

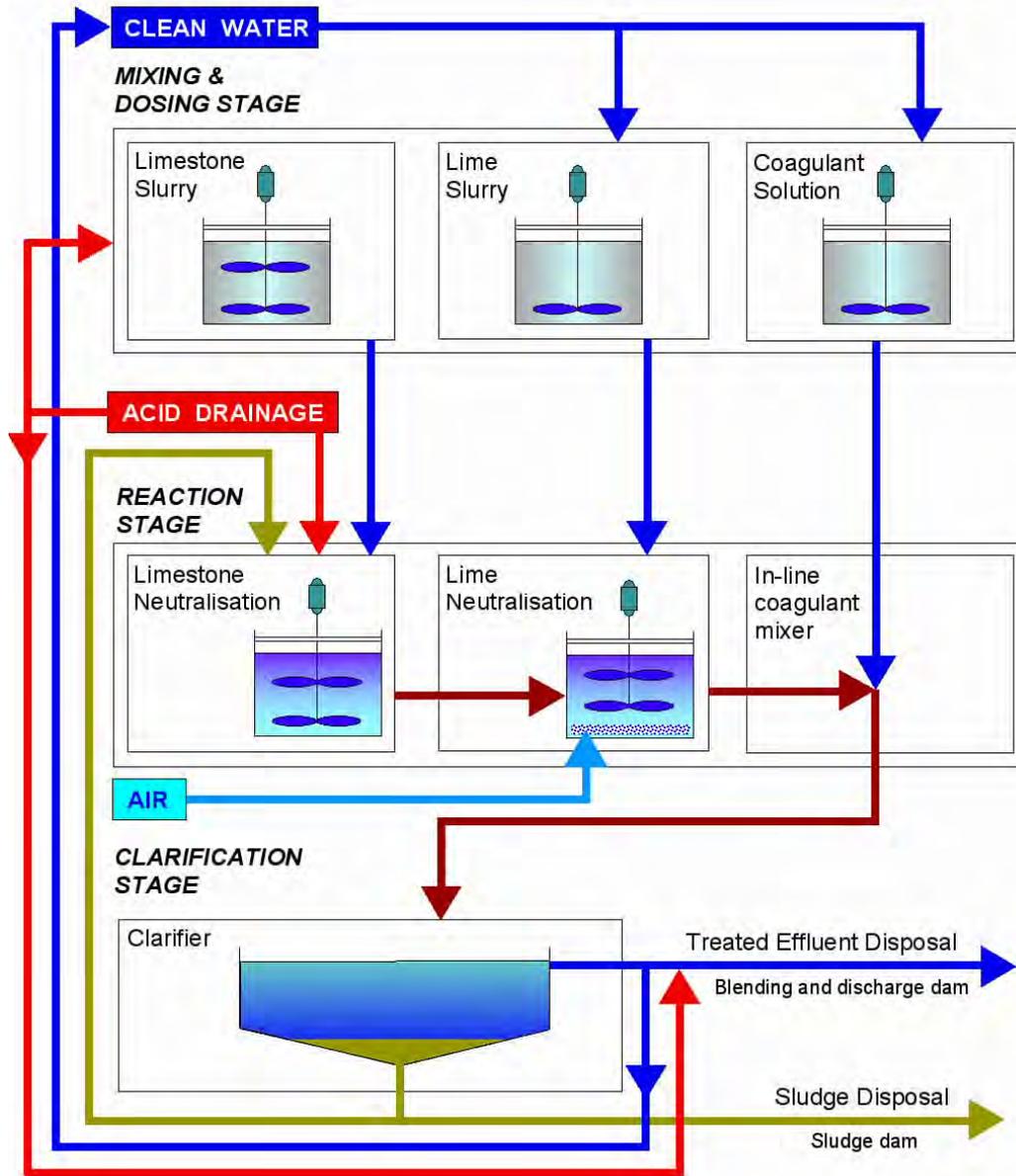


Figure 8. Flow diagram for a typical Low Density Sludge (LDS) or High Density Sludge (HDS) plant for the active treatment of AMD. In a LDS plant, all sludge from the base of the clarifier is disposed. In a HDS plant, a proportion of the sludge is recycled from the clarifier back into one of the reactor tanks, to complete the first stage of neutralisation.

LDS plants can effectively treat AMD with a range of Acidity Loads, however the main disadvantages of these plants are:

- The large volume of low density sludge produced (typically less than 5 wt% solids).
- The substantial storage requirements associated with low density sludge and the requirement for dewatering to increase the sludge density prior to final disposal.
- The costs associated with sludge handling and safe disposal of potentially unstable treatment precipitates.

These issues can be partially addressed with High Density Sludge (HDS) plants, as discussed in the following section.

4.1.2 High Density Sludge Plants (pH control / precipitation)

High Density Sludge (HDS) plants are similar to LDS plants and generally involve three main treatment stages, as described in Section 4.1.1: (i) reagent mixing and dosing stage, (ii) reaction stage and (iii) flocculation and clarification stage. The key difference associated with HDS plants is that a proportion of alkaline treatment sludge from the thickener underflow is recycled back through the plant to complete the first phase of neutralisation. This has the affect of progressively increasing sludge density – sometimes up to 40 wt% solids, as well as improving the efficiency of reagent use. Sludge handling and disposal costs can be significantly reduced by the HDS process, and reagent costs can also be reduced as a result of the improved efficiency of reagent use.

The process flow sheet in Figure 8 illustrates the recycling of sludge from the base of the clarifier/thickener tank (clarification stage) back into the neutralisation reactor tank (reaction stage).

LDS plants can generally be easily converted to HDS operation, for a relatively minor cost in comparison with the initial cost of plant installation.

A fixed LDS plant was recently converted to HDS mode at a decommissioned mine site in South Australia (Plate 10). Alkaline sludge from the clarifier/thickener outlet is used to raise the pH of incoming AMD to near neutral conditions before a neutralisation reagent (eg. hydrated lime) is added in the next stage of treatment. The density of treatment sludge has increased from around 5 wt% solids (LDS) to 30-35 wt% solids (HDS). Modification to the existing plant was completed at minimal cost, and included redirection of a number of pre-existing pipes and installation of an improved aeration system.



Plate 10. High Density Sludge (HDS) plant used for the continuous treatment of AMD from a decommissioned mine site. Key sources of AMD at the site include pit wall rock and benches, waste rock dumps and a tailings storage facility.

4.1.3 Pulsed Carbonate Reactors (pH control / precipitation)

Pulsed Carbonate Reactors (PCR) are based on the principle that increasing the partial pressure of carbon dioxide (CO₂) in water dramatically enhances the solubility of carbonate (eg. limestone).

The dissolution of solid calcium carbonate (CaCO₃) to produce aqueous calcium bicarbonate (Ca(HCO₃)₂) is represented in Reaction 11. This equilibrium indicates that increasing the partial pressure of CO₂ will enhance the dissolution of CaCO₃. Calcium bicarbonate can subsequently neutralise acid according to Reaction 12.

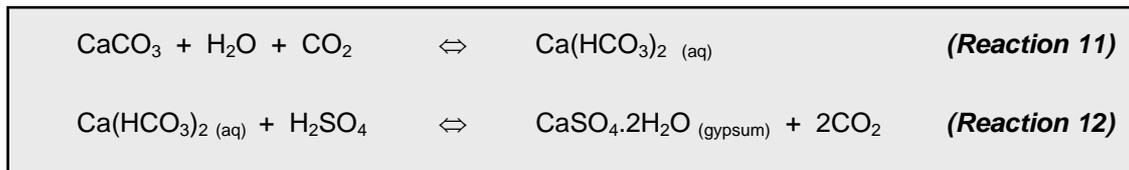


Figure 9 shows a typical flow diagram for a PCR plant. As shown in Figure 9, CO₂ is initially absorbed into the AMD at atmospheric pressure. To further increase the CO₂ content in the AMD, the water is then saturated with CO₂ (at high pressure) from an external source of liquid CO₂.

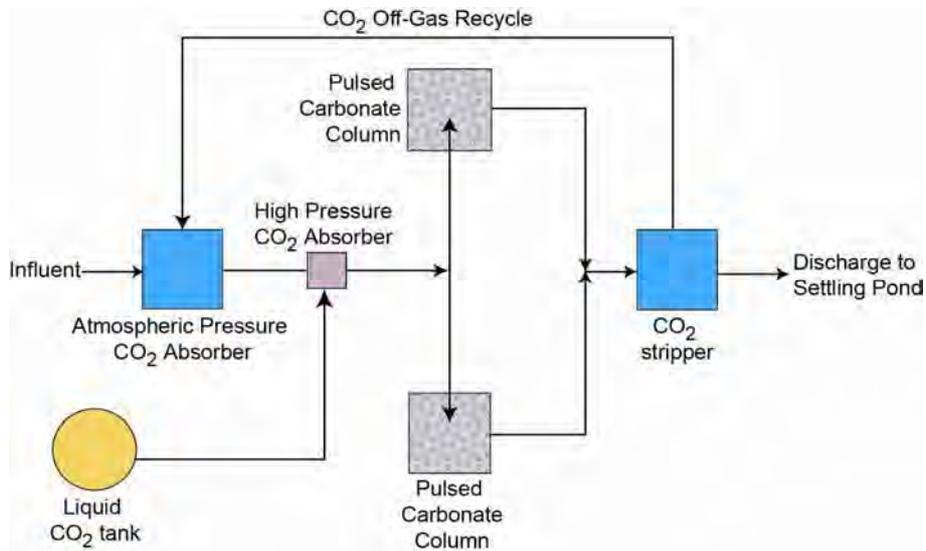


Figure 9. Flow diagram showing key components of a Pulsed Carbonate Reactor (PCR) system for AMD treatment.

The CO₂-saturated AMD is then pulsed through a series of columns/reactors where it is neutralised with calcium carbonate. Dissolved CO₂ in the AMD facilitates the dissolution of CaCO₃ (Reaction 11), which increases the amount of alkalinity that can be generated from CaCO₃, and therefore increases the efficiency of reagent use. By pulsing the CO₂-rich AMD into the carbonate columns/reactors, a high-energy environment is created in the columns,

which promotes particle abrasion and reduces armouring. As the carbonate dissolves and neutralises the AMD, CO₂ pressure builds within the reactors (eg. Reaction 12). The CO₂ can be continuously recirculated within the plant as shown in Figure 9, so that CO₂ produced from Reaction 12 can be used as an input to Reaction 11. This eliminates the need to provide a constant external source of CO₂ during AMD treatment.

Water discharged from PCR plants may require post treatment, such as an aerobic wetland, to permit the evolution of CO₂ and raise the pH of the effluent.

Key benefits of PCR systems include the generation of high levels of alkalinity and efficient use of low cost limestone, although routine limestone replenishment in sealed reactors is not straightforward.

4.1.4 Electrochemical Concentration

Electrochemical techniques use combinations of electrical, magnetic, chemical, and plasma technologies to extract metals from AMD solutions. Emerging electrochemical techniques include: Solvent extraction and electrowinning; Pulsed Plasma Technology; Magneto-Electrochemical technology; Ion Conduction Agglomeration and Alternating Current Electrocoagulation. These techniques are focussed on metal and cost recovery, but none are in routine use for AMD treatment.

4.1.5 Biological Mediation / Redox Control (Sulphate Reduction)

Microbial Reactor Systems (MRS) are fully engineered and process controlled systems for harnessing chemical and biological processes to neutralise AMD and potentially recover metals (De Vegt et al., 1998). Microbial Reactor Systems consist of a sulphate reducing bioreactor and metal sulphide precipitators (Figure 10). In the sulphate reducing bioreactor, bacterial activity reduces sulphate (SO₄²⁻) to soluble H₂S (and HS⁻) and produces HCO₃⁻ (refer to Reaction 9). In the metal sulphide precipitators, HCO₃⁻ partially neutralises the incoming water, while H₂S and HS⁻ react with dissolved metals in the AMD, resulting in precipitation of the metals as sulphide minerals. The precipitation of sulphide minerals is an acid consuming reaction (eg. reverse of Reactions 3, 4, 5 or 6). Partially treated AMD from the metal sulphide precipitators then flows into a limestone reactor for further neutralisation. Water flows from the limestone reactor at near neutral pH into the sulphate reducing bioreactor, where it provides a source of sulphate for the bacterial activity. Treated AMD is then discharged from the bioreactor, while the H₂S, HS⁻ and HCO₃⁻ produced in the bioreactor are circulated into the precipitator.

A benefit of MRS plants is that metal sulphide precipitates are generally less soluble and therefore more stable, in their reduced state, than their corresponding metal hydroxides. Subsequent recovery of commercial metals can be used to defray treatment costs.

MRS plants are best suited to treating AMD with a pH of 3.0-5.5 and ambient oxygen conditions (De Vegt et al., 1998). The successful performance of MRS is reliant on the

continued growth of sulphate reducing bacteria (SRB), which require temperatures between 5 and 40°C, pre-treated pH levels above 5.5 and redox potential (ORP) levels below +150 mV. Commercial MRS plants for AMD treatment are rare.

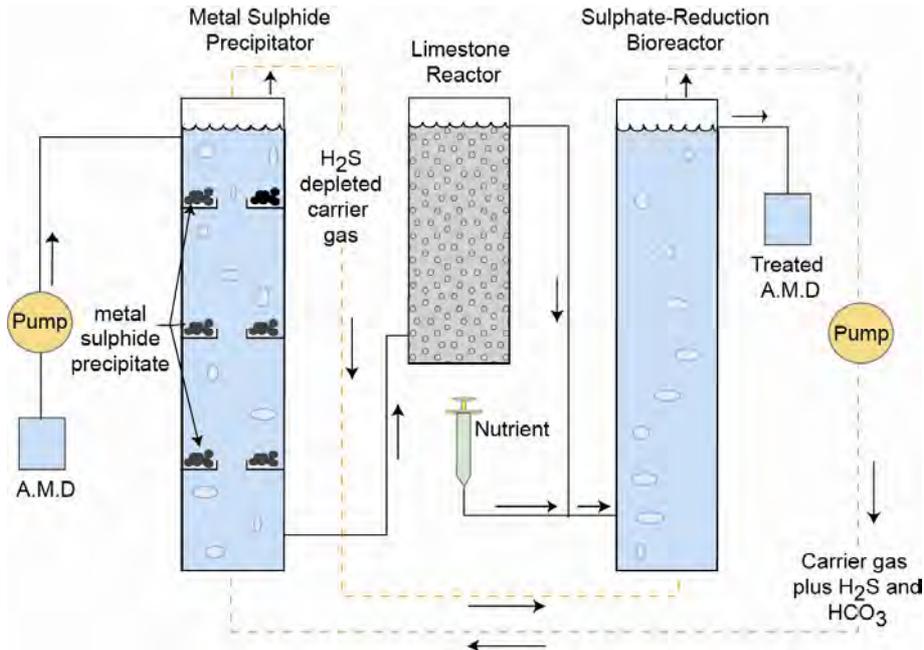


Figure 10. Flow diagram showing key components of a Microbial Reactor System (MRS) for AMD treatment.

4.1.6 Ion Exchange / Absorption or Adsorption / Flocculation and Filtration

Toxic metals can substitute for harmless ions in natural or synthetic zeolites or a variety of synthetic resins. Many ion exchange technologies appear to be technically effective at achieving water quality targets, but few have proven to be commercially viable or are in widespread use at this time. A range of silica-based and polymeric resins currently in use or at various stages of development can be used for metal recovery or removal. The economic viability of these techniques is limited.

4.1.7 Crystallisation

Crystallisation is a treatment process that may be used to decrease sulphate concentrations in AMD. The influent AMD must be pre-treated to adjust the pH and decrease metal concentrations prior to commencing the crystallisation treatment process.

Residual sulphate concentrations are commonly elevated in effluent from conventional active treatment systems, and are typically associated with dissolved Ca and Mg in the treated

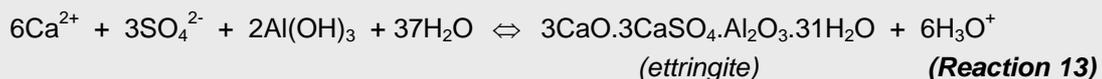


water. Elevated sulphate can be a particular issue if Mg-based neutralisation reagents (eg. $\text{Mg}(\text{OH})_2$, MgCO_3) are used rather than Ca-based reagents (eg. $\text{Ca}(\text{OH})_2$, CaCO_3) due to the relatively high solubility of MgSO_4 in comparison with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Nevertheless, not all treated waters are saturated with respect to gypsum.

The “Savmin” and “Wren Hydrothermal” processes offer new methods for lowering soluble sulphate concentrations in water that has already been subjected to conventional hydrated lime ($\text{Ca}(\text{OH})_2$) treatment. It is possible to lower sulphate concentrations to below 200 mg/L with these approaches.

“Wren Hydrothermal” technology involves pre-treatment of AMD using hydrated lime ($\text{Ca}(\text{OH})_2$) to raise the pH of incoming water to 11 and provide an initial reduction in sulphate concentrations (eg. from 3,000 mg/L to approximately 1,400 mg/L; Stenzel and Günther, 2005). Subsequently, the pre-treated AMD is transferred to a reactor where high temperatures and pressures are used to promote further precipitation or “crystallisation” of CaSO_4 (anhydrite). This crystallisation process decreases sulphate levels to below 200 mg/L (Stenzel and Günther, 2005).

“Savmin” is an alternative technology, which uses chemical rather than hydrothermal processes, to promote the crystallisation of sulphate minerals. As described in Sibilski (2001), the first stage of the Savmin process involves raising the pH to 12.0-12.3 using hydrated lime, to precipitate heavy metals and magnesium as hydroxides. In the second stage, the solution is contacted with gypsum crystals which provide active surfaces to catalyse the precipitation of more gypsum, which is then removed by thickening or filtration. The third stage involves addition of aluminium hydroxide ($\text{Al}(\text{OH})_3$) to the remaining solution, which results in the precipitation of Ca, SO_4 and Al in the form of ettringite (Reaction 13).



In the fourth and fifth stages of treatment, ettringite is separated from the solution and $\text{Al}(\text{OH})_3$ is regenerated. The ettringite slurry is decomposed by adding sulphuric acid to enable recycling of $\text{Al}(\text{OH})_3$ (reverse of Reaction 12), while the remaining solution continues to the final stage of the treatment process (see below). The solution produced during decomposition of the ettringite slurry becomes saturated with respect to CaSO_4 , and is then mixed with gypsum seed crystals to optimise gypsum precipitation. A solution dominated by soluble Al remains, and is recycled within the system.

The final stage of the Savmin process involves treatment of the solution that remains after removal of the ettringite slurry. This part of the process involves addition of CO_2 to lower the pH to a suitable level. This results in CaCO_3 precipitation, which is then filtered from the treated solution.

4.2 In-situ AMD Treatment

In-situ treatment systems generally use pH control/precipitation methods for the treatment of AMD. Table 16 provides a list of typical *in-situ* treatment applications.

In-situ dosing systems are generally small, portable plants with relatively low capital costs. All portable dosing systems have storage and dispensing capabilities and use similar reagents, such as calcium hydroxide (Ca(OH)₂). Portable systems can be fully automated or manual. The equipment can be modified to suit site-specific needs, with multiple treatment tasks being performed with a single unit. These systems are well suited to sites where the infrastructure and operating costs of piping and pumping AMD back to a central plant are exceeded by the costs of a portable system. The prime function of portable dosing systems is to meet discharge requirements by raising the pH of water and lowering soluble metal concentrations.

The most common applications of portable dosing systems are:

- Emergency response or other short-term treatment applications where a large quantity of reagent needs to be dosed into a water body or stream over a short period of time.
- Long-term treatment applications where a relatively low dose rate is required over an extended period of time.

Portable systems are limited by the requirement for power, cost and regular replenishment of reagent, routine maintenance, and issues relating to sludge disposal. One of the main disadvantages of *in-situ* treatment in AMD-affected channels or streams is that sludge may be transported and deposited downstream of the treatment location. Treatment sludge is generally less of an issue for open water bodies (eg. pit lakes), as the treatment precipitates can remain on site, settling to the bottom of a water body, and sometimes eliminating the need for sludge handling and disposal.

A number of portable systems are currently used to treat AMD, as described in the following sections.

Table 16. Typical applications for active in-situ treatment of AMD.

<i>In-situ</i> AMD treatment applications	
Process water ponds	Waste rock pile discharges
Heap leach ponds	Groundwater seepage discharges
Pit lakes	Groundwater dewatering discharges
Tailing dams	Adit discharges
Stormwater ponds	Channels, creeks, rivers



4.2.1 Neutra-Mill Dosing Systems

Small, dry-reagent mixing and dosing systems employing Neutra-Mill technology, developed by Earth Systems, provide the reagent dispensing capacity of a large fixed plant system in a basic, mobile unit (Plates 11-12). The portability of these systems enables them to be transported to AMD sources, rather than pumping water to a fixed plant. This approach offers greater flexibility and significantly lowers the capital and operating costs of treatment tasks.

The Neutra-Mill is a portable, water- or land-based dry reagent dosing system that consists of a rotating, cylindrical, stainless steel mixing chamber. In the water-based systems, the mixing chamber is partially submerged allowing water to flow through freely. The drum rotates around a horizontal central axis, and is powered by an electric motor, gear box and pulley assembly. Chemical dispensing rates from the drum are controlled by varying its speed of rotation.



Plates 11-12. The Neutra-Mill can be used for in-situ (active) treatment of large open water bodies, such as pit lakes, or streams affected by AMD. The equipment can be water-based (above) or land-based (right), and does not require manual operation.



4.2.2 Calibrated Reagent Applying Blender (CRAB) Dosing Systems

The CRAB system (developed by Acid Solutions Pty Ltd) is a portable, generator-powered, reagent dosing system, which consists of a reagent storage hopper, delivering/metering system, and a mixing/dispensing system (Plate 13).

The CRAB system has similar applications to the Neutra-Mill technology described above. For example, the CRAB system can be installed in remote locations and is suited to both small and large scale treatment applications.



Plate 13. Calibrated Reagent Applying Blender (CRAB) system.

4.2.3 Aqua-fix Systems

Aqua-fix treatment systems (developed by Aqua-fix Systems Inc.) include portable and fixed plant pebble quicklime (CaO) dosing systems. In remote areas where external power supplies may not be available, the portable units can be operated using water power alone. A water wheel activates the release of a stream of dry powdered pebble quicklime directly into flowing water beneath the unit (Plate 14). Without the need for an external power supply, Aqua-fix systems are well suited for remote sites and automatic operation. Maintenance requirements are minimal. Like all *in-situ* treatment systems, replacement of reagent is required.



Plate 14. Aqua-fix system treating AMD from a waste rock pile.

In-situ treatment using the water powered Aqua-fix systems involves the deposition of metal hydroxide sludge in the waterway being treated. For effective operation of Aqua-fix systems, the quicklime reagent must have a uniform grain size that enables a steady flow of grains through the hopper and into the AMD-affected stream. Thus, specific reagent requirements limit the applications of these systems.



4.2.4 Hydro-Active Limestone Treatment (HALT) Systems

The HALT system (Plate 15) was developed to overcome the problem that many treatment systems face in trying to use limestone efficiently and minimise armouring. Locally available limestone gravel (eg. 10-15 mm aggregate) is stored in a hopper and automatically fed into a subaqueous ball mill. The mill grinds the aggregate under water and produces ultra-fine particles (eg. 30 wt.% of particles $<0.5 \mu\text{m}$) of highly reactive limestone at a controlled rate, helping to overcome armouring issues. HALT Systems provide the benefit of using environmentally benign, very low cost limestone aggregate, delivering up to 50 tonnes of



Plate 15. This portable land-based HALT mill can be used for in-situ (active) treatment of large open water bodies, such as pit lakes, or streams affected by AMD.

limestone per day, but cannot achieve a pH greater than 7.5-8.0. HALT Systems require careful engineering to respond to flush events.

Portable HALT systems are designed for automated and continuous operation, and they can be installed and operational within 24 hours. Systems with the capacity to deliver more than 5 tonnes of limestone per day can be considered as fixed plants.

5. Conclusions

Acid and metalliferous drainage (AMD) is a major issue affecting metal and coal mining operations worldwide. AMD is typically characterised by low pH and elevated metal and sulphate concentrations. However, not all AMD has low pH, as Acidity is present in near neutral pH waters containing high metal concentrations.

If AMD formation cannot be prevented, then minimisation strategies and/or treatment of AMD is required. Treatment technologies are commonly categorised as either “passive” or “active”, with most systems utilising aggregate carbonate or lime-based reagents.

Passive treatment systems are almost invariably used for post closure treatment scenarios, and are best suited to AMD with low Acidity (<800 mg CaCO₃/L), low flow rates (<50 L/s) and therefore low Acidity Loads (<100-150 kg CaCO₃/day).

Active treatment systems generally require routine addition of reagent and regular maintenance and, unlike their passive counterparts, can be engineered to accommodate essentially any Acidity, flow rate and Acidity Load. Active treatment of AMD can be achieved using fixed plants or portable equipment for *in-situ* treatment. *In-situ* treatment becomes a viable option when the cost of diverting AMD to a fixed plant exceeds the cost of building a smaller, portable plant.

Successful treatment requires site-specific installation and implementation, along with selection of technology appropriate to the chemistry and Acidity Load of the AMD. However, there are categorically no walk-away treatment solutions. All treatment systems require some form of maintenance and/or regular reagent addition. Correctly selected treatment systems that are poorly installed or utilised can be just as ineffective as inappropriately chosen treatment systems.

The key factors in selection and design of active and passive AMD treatment systems are: (i) water chemistry (including pH, metals, sulphate levels and redox state) and flow rate of influent AMD, and (ii) the objectives of AMD treatment (eg. protection of site infrastructure, downstream aquatic ecosystems or water resources). Other important factors include capital and operating costs, availability of suitable treatment reagents/materials and sludge management issues.



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