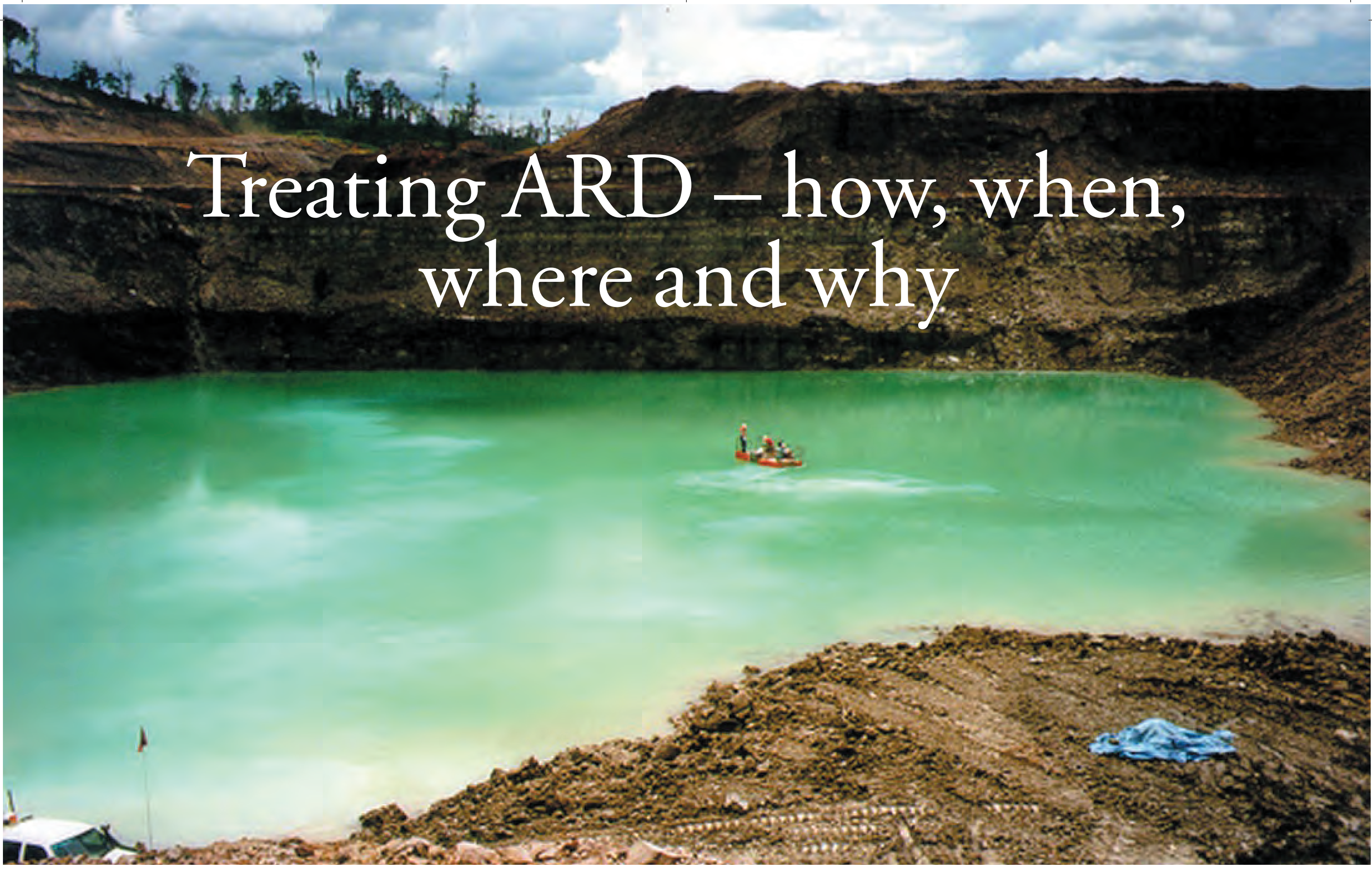


Treating ARD – how, when, where and why

Acid rock drainage (ARD) is a major issue affecting both the environment and the economics of metal and coal mining operations worldwide. ARD is formed when rocks containing some sulphide minerals are exposed to air and subsequently leached. The drainage is a near neutral or low pH cocktail of dissolved metals and sulphate-rich water.

ARD can have significant impacts on the economics of a mining operation. This is due to the corrosive effects of acid water on infrastructure, the limitations it places on water reuse and discharge and the expense incurred implementing effective closure options. While ARD minimisation and control must remain the focus of mine-site water management strategies, when acid generation is unavoidable, appropriate passive or active treatment technologies need to be implemented. Treatment technologies are commonly categorised as either passive or active. The main purpose of both types is to lower total acidity, raise pH and lower toxic metal and sulphate concentrations.

Passive treatment systems take advantage of installed chemical and biological processes. Passive approaches are economically attractive, but have some significant limitations. They are best suited to the treatment of waters with low acidity (<800 mg $CaCO_3$/litre), low flow rates (<50 litres/s) and therefore low acid loads, where the key chemical outcome is a near neutral pH. With only a few exceptions, passive systems cannot handle acid loads in excess of 100-150 kg of $CaCO_3$ 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 ARD issues, particularly at some coal mines. It is critical that they be deployed within their chemical and physical limitations. While passive treatment systems have always been regarded as providing lower cost solutions, the inappropriate application of such

Floating water treatment systems are often ideal for pit lake treatment. Treatment is being conducted in a flooded open cut at a coal mine in Indonesia.

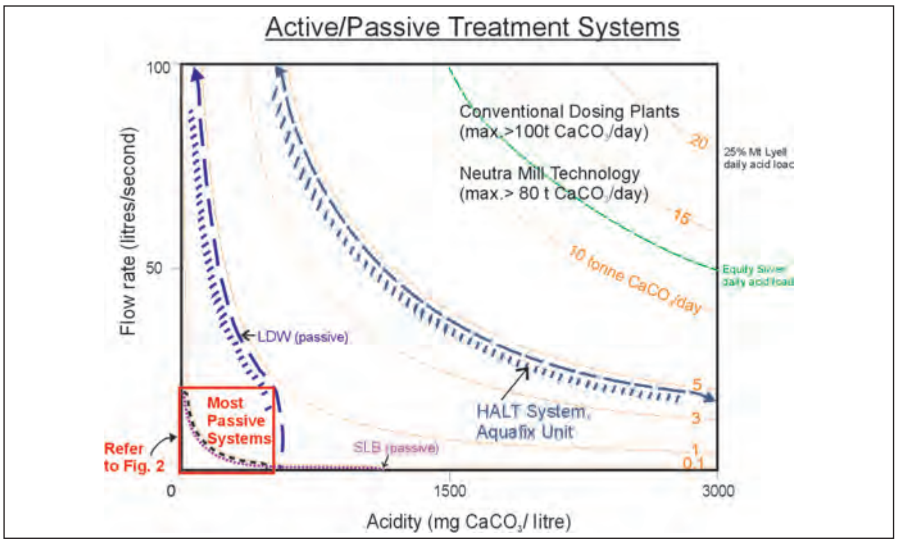


Figure 1: Acid load guidelines for selecting effective active and passive treatment systems. Contours shown are for acid loads in tonne $CaCO_3$/d. Daily acid loads associated with two well known mine sites are included for reference. The capability fields of passive treatment systems has been expanded in Figure 2.

Table 1: Broad guidelines for determining the suitability of passive and active treatment systems based on influent water characteristics.

	Av. Acidity Range (mg $CaCO_3$/litre)	Av. Acid Load (kg $CaCO_3$/d)	Av. Flow Rate (litres/s)	Typical pH range	Max pH attainable
Passive	1 - 800	1-150	< 50	> 2	7.5
Active	1 – 10,000	1,000-50,000	No Limit	No Limit	14

systems has resulted in many being far more costly than conventional active treatment plants.

Unlike their passive counterparts, active treatment systems can be engineered to accommodate essentially any pH, flow rate and daily acid load. Although not limited by tight operational parameters as in the case of passive systems, the unlimited chemical flexibility of active treatment systems comes at a price. Economic considerations (ie. capital and ongoing operating cost) play a big role in determining the viability of active treatment systems. Table 1 shows some fundamental differences between the capabilities of passive and active systems.

On a plot showing ARD flow rates (in litres/s) versus acidity values (in mg $CaCO_3$/litre), the treatment capability 'fields' for a range of passive and active treatment systems are shown in Figure 1. Contours on this plot show daily acid loads in tonnes of $CaCO_3$. The fields for most passive treatment systems lie in the boxed potion in the lower left hand corner of this plot and this area is expanded to show more detail in an identical plot in Figure 2.

PASSIVE TREATMENT

Passive treatment systems cannot be regarded as walk-away solutions. However, the correct implementation of a passive system will maximise the life of the system. At present, passive systems are almost invariably used for post closure, low acid load treatment scenarios, not for operating mine sites.

The formation of precipitates and armouring of limestone by metal hydroxides and gypsum is a key problem that can greatly reduce the effectiveness of limestone-based passive treatment systems. As well as clogging flow

Table 2: Summary of Abbreviations for Figures 1 and 2.

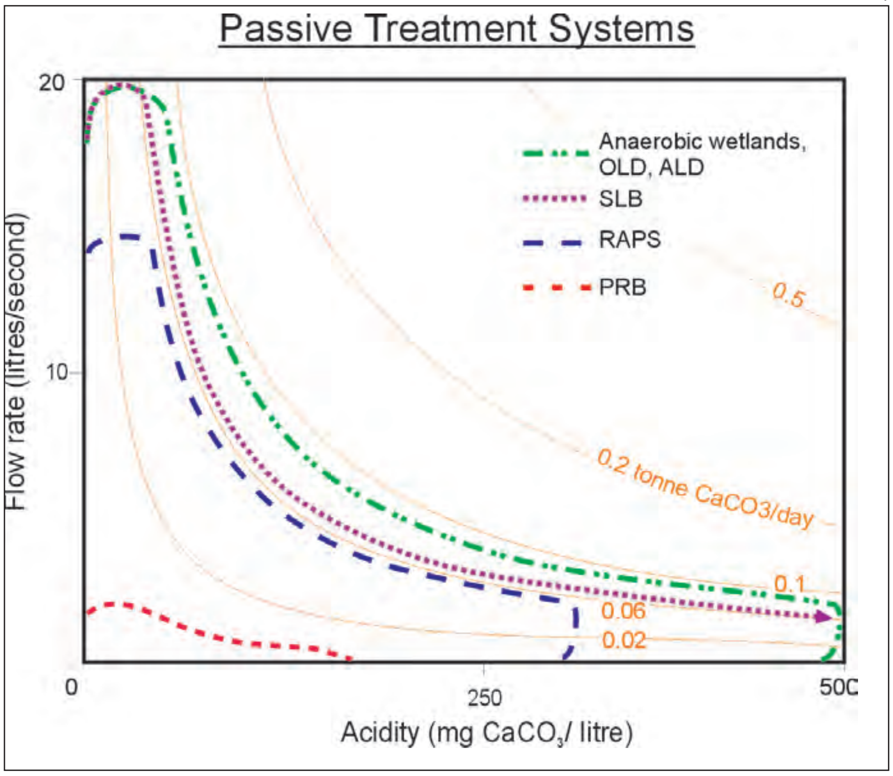
ALD,	Anoxic limestone drains,
OLD	Oxic limestone drains
SLB	Slag leach beds
RAPS	Reducing and alkalinity producing systems
PRB	Permeable reactive barriers
LDW	Limestone diversion wells
HALT	Hydro active limestone treatment

Portable, water-based treatment systems are often ideal for emergency response and one-off water treatment tasks. They can be mobilised over the water body or moored in one location during treatment.

pathways through the substrate, armouring also retards the reactivity of limestone. Armouring can be at least partially overcome by approaches that minimise the presence of oxygen within the treatment system, maximise the available surface area of the limestone and/or provide sufficient agitation within the system for the continuous abrasion of armoured surfaces.

Oxic Limestone Drains (**OLD**) are channels containing coarse limestone aggregate[1]. 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. They can be constructed to channel flows or implemented within existing drainage lines. OLDs are best suited to treat ARD with pHs above 2, acidities below 500 mg $CaCO_3$/litre, flow rates of less than 20 litres/s, and total acid loads less than 150 kg $CaCO_3$/d (see Figure 2).

Figure 2: Acid load guidelines for selecting effective passive treatment systems. Contours shown are for acid loads in tonne $CaCO_3$/d. See Table 2 for abbreviations.



Anoxic Limestone Drains (**ALD**) are buried trenches of coarse limestone aggregate layered in carefully constructed drainage lines along gently graded slopes[2]. Low oxygen conditions are maintained within the drain in order to avoid oxidation and precipitation of ferric hydroxide. ALDs have been shown to be most effective for influent water having a pH above 2, an acidity below 500 mg/litre, a flow rate of less than 20 litres/s, a dissolved oxygen concentration of less than 1 mg/litre and an acid load of less than 150 kg $CaCO_3$/d, (see Figure 2).

Limestone Diversion Wells (**LDW**) are an option in environments that offer a suitable topographic fall. They consist of a well (e.g. an in-ground metal or concrete tank) that contains crushed limestone aggregate. Part of a fast flowing acid stream is diverted, often via a pipeline, into the well[3,1]. The hydraulic force causes attritional grinding and abrasion of the limestone gravel, ensuring that armouring of the aggregate is prevented and a that a fine-grained limestone slurry overflows from the top of the well back into the main body of the acid stream. Limestone diversion wells are suitable for treating ARD with a pH above 2, flow rates of less than 1,000 litres/s, acidity values less than 500 mg/litre, oxygen concentrations close to equilibrium with the atmosphere, and daily acid loads between 100 and 1,000 kg $CaCO_3$/d.

Reducing and Alkalinity Producing Systems (**RAPS**) are a range of broadly similar approaches that have been devised to treat low acidity, low flow, low acid load, relatively reduced ARD flows. These include Alkalinity

Producing Systems, Successive Alkalinity Producing Systems, Vertical Flow Wetlands and Reverse Alkalinity Producing Systems (see Figure 2). 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[4,5]. Such systems:

1. Utilise mixtures of limestone and organic matter and thereby represent combined inorganic and organic approaches to ARD treatment
2. Rely on alkalinity generation via limestone dissolution and sulphate reducing bacterial (SRB) activity
3. Enhance reducing conditions (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.

RAPS can be used when initial dissolved O_2 concentrations are up to 3 mg/litre. The successful performance of these systems requires the influent ARD to have a pH above 2.5, an acidity below 300 mg/litre as $CaCO_3$, an average flow rate of less than 15 litres/s and acid load generally below 100 kg $CaCO_3$/d. Although placed in a separate category (below), anaerobic wetlands are also a type of RAP system.

Pyrolusite limestone beds consist of shallow, limestone-filled channels that permit substantial residence time for manganiferous water. The limestone is inoculated with aerobic micro-organisms (generally algae) that accelerate the oxidation of the affected water. Pyrolusite limestone beds are best suited where the majority of the acidity is related to soluble manganese concentrations[3]. Appropriate water could have a pH between 3 and 7 with an acidity below 500 mg/litre $CaCO_3$, and an oxygen concentration as close as possible to saturated with respect to atmospheric oxygen. Initial data suggests that practical acid load limitations are likely to be in the 100-500 kg $CaCO_3$/d range.

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[2,4,6]. Key factors that need to be considered when determining the type, size and cost of an appropriate wetland system include:

◆ The influent acidity loads, pH and redox state
◆ Water flow rates and retention times
◆ The area available for a wetland.

Aerobic wetlands require the influent acid load to be below 1 kg acidity as $CaCO_3$ per 300 m^2 of wetland/d[2]. The pH of the in flowing drainage has to be above 6 and dissolved oxygen concentrations need to have reached saturation with respect to the atmosphere early within the residence time of the water in the wetland.

Acid drainage ponding on the tailings contaminated bank of a river in Tasmania, Australia.

Anaerobic wetlands are best suited to treat ARD that contains an acid load of 1 kg acidity as $CaCO_3$ per 200-500m^2/d[2]. The pH of influent should generally be 4.0 or higher, and while ambient oxygen concentrations can be tolerated, more reducing conditions favour extended life expectancies (Figure 2).

Permeable Reactive Barriers (PRB) are buried beds of reactive material that are designed to intercept groundwater plumes of ARD to assist with *in-situ* remediation (see Figure 2). Three types of PRBs suitable for ARD treatment are Organic Rich Barriers (ORB), Slag Leach Beds (SLB) and an emerging technology, Zero Valent Iron (ZVI) barriers. Limited data suggests that effective organic-rich PRBs require influent pH levels above about 4-4.5, relatively low oxygen concentrations (e.g. <3-4 mg/litre), flow rates of less than 10litres/s and daily acid loads of less than 10-30 kg $CaCO_3$/d (see Figure 2). Barriers of this type are not suitable for installation in cold climates as low soil temperatures (<5°C) inhibit bacterial activity. Ongoing maintenance of the PRB, including replacement of barrier materials, is required.

Gas Redox and Displacement System (GaRDs) is an emerging passive technique for dealing with ARD from underground mines currently undergoing a field demonstration in Australia. The GaRDs retards sulphide oxidation by displacing oxygen from underground workings[7]. GaRD systems are expected to be useful where flooding of underground workings is not feasible, or where pressure bulkheads are undesirable. The air is displaced from the mine voids with a reducing gas mixture comprising carbon dioxide and methane, which can be generated in an external anaerobic bioreactor, or via coalbed methane. Since this approach is designed to stop sulphide oxidation, it can ideally be applied to any acid load situation.

ACTIVE TREATMENT

A broad range of active treatment approaches are available for dealing with ARD. Physical, chemical and biological approaches include one or more of the following:

1. pH control or precipitation
2. Electrochemical concentration
3. Biological mediation/redox control (sulphate reduction)
4. Ion exchange/absorption or adsorption/flocculation and filtration
5. Crystallisation.

pH Control/Precipitation with inorganic alkaline amendments is the most common and cost effective form of general purpose ARD treatment. A large variety of natural, manufactured or by-product alkaline reagents are available, with their use generally dictated by availability and cost. Alkaline reagents treat ARD by increasing the pH and promoting the precipitation of heavy metals, generally as hydroxide complexes.

The successful implementation and the sustainability of 'pH control' active treatment systems requires the selection of a reagent appropriate for the treatment task and an efficient mixing and dispensing mechanism. Conventional alkaline reagents used to treat ARD include hydrated lime, quicklime, caustic soda, soda ash, ammonia, magnesium oxide, mineral carbonates (e.g. limestone, dolomite, magnesite and witherite) and silica micro encapsulation reagents.

Less known alkaline amendments include lime and cement kiln dust, fly-ash, fluidised bed combustion ash, calcium peroxide, potassium hydroxide and seawater neutralised red mud (from bauxite processing).

A wide variety of general purpose and proprietary, fixed-plant, dry powder and liquid mixing and dosing systems are available for the treatment of ARD. The principal benefit of conventional neutralisation plants is that they can be engineered to handle any acid load or unexpected eventuality and achieve most water quality targets (see Figure 1). 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 ARD sources. Significant additional costs are incurred when the ARD source is some distance from the plant. These costs are associated with piping and pumping acid flows over long distances, especially in mountainous terrain.

Small, dry reagent mixing and dosing systems employing Neutra-Mill technology provide the reagent dispensing capacity of a large fixed plant system in a basic, mobile unit. The portability of these systems enables them to be transported to ARD 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. Portable treatment systems such as these are well suited to sites where the infrastructure and operating costs of piping and pumping ARD back to a central plant are exceeded by the costs of the portable system.

Aquafix systems are portable and fixed plant pebble quicklime dosing systems. The units operate on water power alone. A spinning water wheel activates the release of a stream of dry powdered pebble quicklime directly into flowing water beneath the unit. Without the need for an external power supply, Aquafix systems are well suited for remote sites and automatic operation. Maintenance requirements are minimal.

The HALT (Hydro-Active Limestone Treatment) system was developed in response to the problems that passive treatment systems face in trying to use limestone efficiently. Locally available limestone gravel (e.g. 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 (e.g. 30 wt.% of particles <0.5 μm) of highly reactive limestone at a controlled rate. HALT systems provide the benefit of using environmentally benign, very low cost limestone aggregate, but cannot achieve a pH greater than 7.5.

Pulsed Carbonate Reactors are based on the principle that increasing the partial pressure of carbon dioxide in water dramatically enhances the solubility of carbonate. Acid drainage is initially saturated with carbon dioxide (at atmospheric pressure) from an external source. The CO_2 saturated ARD is pulsed through a series of carbonate-filled columns/reactors, creating a high-energy environment that promotes particle abrasion and reduces armouring. As the carbonate dissolves and neutralises the ARD, CO_2 pressure builds within the reactors. Following treatment in the columns, the carbon dioxide can be recirculated. Key benefits of these systems include the generation of high levels of alkalinity and efficient use of low cost limestone, but routine limestone replenishment in sealed reactors is not simple.

Electrochemical concentration techniques use combinations of electrical, magnetic, chemical, and plasma technologies to extract metals from ARD solutions. Emerging electrochemical techniques include: solvent extraction and electrowinning; pulsed plasma technology; magneto-electrochemical technology; ion conduction agglomeration and AC electrocoagulation. These techniques are focussed on metal and cost recovery, but none are in routine use for ARD treatment.

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 ARD and potentially recover metals[8]. Systems consist of a sulphate reducing bioreactor and metal sulphide precipitators. MRS are best suited to treating ARD with pHs between 3 and 5.5 and ambient oxygen conditions[8]. The successful performance of MRS is reliant on the continued growth of sulphate reducing bacteria, which require temperatures between 5 and 40°C, pre-treated pH levels above 5.5 and Eh levels below 150 mV. Commercial MRS for ARD treatment are rare.

Ion Exchange/Absorption or Adsorption/ Flocculation and Filtration use the fact that 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.

Crystallisation – the 'Savmin' (*MEM*, November 2000, pp.7-9) and 'Wren Hydrothermal' processes offer new methods for lowering soluble sulphate concentrations in water that has already been subjected to lime treatment. It is possible to lower sulphate concentrations to below 200 mg/litre with these approaches.

CONCLUSIONS

Successful treatment relies on the selection of an appropriate technology for the task, as well as its correct implementation. pH adjustment, lowering metal loads and meeting specific discharge standards can be vastly different tasks requiring significantly different technologies: what are you trying to achieve? For most sites, successful technologies will require site specific installation and implementation to achieve maximum benefit. Correctly selected treatment systems that are poorly installed or utilised can be just as ineffective as inappropriately chosen treatment systems.

The operational parameters of most passive treatment techniques are limited to low acid load and almost invariably post closure situations. Passive systems generally do not handle the peak flush events that typify many ARD scenarios. In addition, all passive systems contain a finite quantity of carbonate and/or organic matter and as such they have a limited life span. Passive treatment systems are often incorrectly viewed as walk away solutions to ARD problems. In reality they require ongoing maintenance. The key parameters that influence their operational life expectancy are the influent acid load per unit time relative to the installed alkalinity, and the capacity of the system to store precipitates (porosity) before flow is substantially impeded.

Active treatment systems are not limited to low acid load ARD issues, so they are generally more expensive to maintain than passive systems. The most widely used active treatment approach is pH control with alkaline amendments. The largest single cost component in many active treatment tasks is the reagent. Significant effort should therefore be directed at identifying technologies that improve the efficiency of reagent use, or that use low cost reagents. For most reagents, key strategies include minimising the armouring of reagents with precipitates and preventing saturation of the reagent during dispensing.

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 ARD treatment. Active treatments using calcium based reagents (particularly limestone) are likely to remain the prime choice for neutralising ARD due to their non-proprietary nature, widespread availability, ease of application and cost effectiveness.

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