Are We Making Progress In The Treatment of Acid Mine Drainage?

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Abstract

The formation of acid mine drainage (AMD) during the exposure of sulphide bearing material to oxygen and water, is of a major concern to the global mining industry and the environmental agencies of many nations. The recognition of AMD as one of the more serious current environmental problems internationally has resulted in its causes, prediction and treatment becoming the focus of a number of research initiatives commissioned by governments, the mining industry, universities and research establishments with input and support from environmental lobby groups.

Available literature contains a plethora of patented technologies and treatment techniques to address the growing concern of AMD. The High Density Sludge (HDS) process is cited as the most widely used process internationally to treat large quantities of polluted mine water. This is the most economical process available for the neutralisation of the acid content and the removal of the majority of metals from solution by lime addition. However it leaves between one and two grams per litre of sulfate in the product water and therefore ought to be followed by further treatment steps to reduce the sulfate content. For this, a number of options exist such as reverse osmosis, ettringite based precipitation and biological sulfate reduction.

AMD treatment requires (a) acid neutralisation, (b) metal removal and (c) sulfate removal. The HDS processes, whilst used extensively, addressed (a) and (b) only. This paper aims to provide a review of the current status of technologies aimed at (c) sulfate removal. This paper will also address why these technologies have not gained the same popularity as the HDS process for large scale implementation.

From this review it can be concluded that there are a number of factors that could hinder the technology transfer of treatment options from pilot to large scale implementation including (i) the quest for a "silver bullet" treatment approach versus intelligent solutions integration (ii) the impact of legislative framework and political systems on the selection of treatment options, (iii) the economic impacts of treatment costs and (iv) the treatment of secondary waste production.

Keywords: acid mine drainage, sulfate removal, water treatment technologies.

Introduction

Acid Mine Drainage (AMD) is produced when sulfide-bearing material is exposed to oxygen and water. This process can occur naturally, being mainly a function of the mineralogy of the local rock material and the availability of oxygen and water (Akcil, 2005). However mining can accelerate the process by exposing sulfide surfaces in mine waste rock, tailings and mine structures for example pits and underground workings. Naturally occurring bacteria promote AMD formation by catalysing the breakdown of sulphide minerals which they utilise as an energy source.

AMD is a historical problem that is worsened by present mining practices. It can potentially occur indefinitely and the long term environmental impact will continue long after mining activities have ceased. There are many abandoned, derelict and defunct mines which are a threat as gradually rising water is flooding these mines. This results in the contamination of shallow groundwater and surface water resources which is important for agriculture and human consumption.

A number of water treatment technologies have been proposed for AMD treatment, each producing a different quality of product water. It is important when choosing an AMD treatment technology that the end use of the product water has been identified first. For example some typical applications of treated water and the required sulfate levels thereof are given in Table 1.

The cost effectiveness of the process and the waste streams it will generate are also critical factors when choosing a suitable AMD treatment technology. The different technologies which have been evaluated can be divided into the following categories:

a. Chemical treatment processes with precipitation;
b. Biological sulfate reduction;
c. Physico-chemical treatment processes.

Background to AMD

AMD production

Typically AMD has a low pH, high conductivity, high concentrations of iron, aluminium and manganese, and low concentrations of toxic heavy metals. The reactions for acid production are best described by the oxidation of pyrite (FeS_2). The simplified pathway for pyrite oxidation is shown in Figure 1.

The equations described above have assumed that the oxidized material is pyrite and that the oxidant is oxygen. There are however other sulphide minerals such as pyrrhotite (FeS) and chalcocite (Cu_2S) which can also contribute to AMD generation.

Chemical treatment processes with mineral precipitation

SAVMIN™

SAVMIN™ was patented by Mintek in 1998 for the treatment of AMD. A key feature of SAVMIN™ is that it is able to decrease sulfate concentrations to less than 200 mg/L SO_4^{2-} via the addition of aluminium hydroxide to form the highly insoluble ettringite precipitate. A demonstration plant was recently run at Sibanye- Stillwater. An aerial view of the demonstration plant is shown in Figure 2.

Figure 2 *Aerial view of SAVMINTM demonstration site*

Table 1. Acceptable sulfate levels for potential applications of product water (Oelofse, 2012)

Product water application	Acceptable sulfate level in mg/L
Coal processing plant	1000
General industrial use	500
Discharge to public streams	500
Irrigation	200
Potable use	200
Cooling water in power station	20-40

$$FeS_2 + 7/2\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$Fe^{2+} + ¼\,O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\,(solid)} + 3H^+$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Overall reaction

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$$

Figure 1 *Simplified pathway for pyrite oxidation*

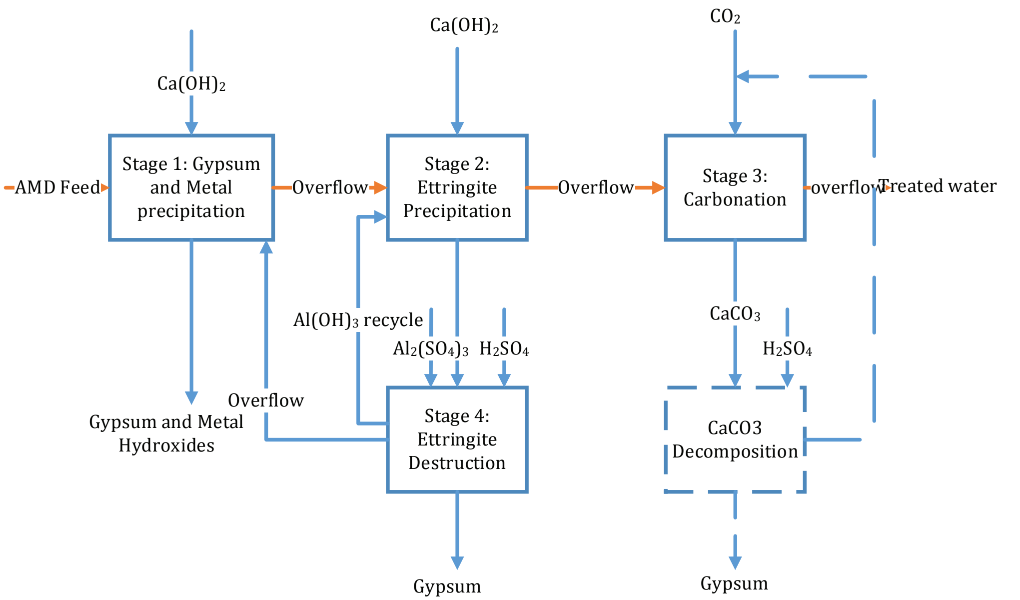

Figure 3: Simplified block flow diagram of SAVMINTM

A simplified block flow diagram of SAVMIN™ is shown in Figure 3. There are four stages in SAVMIN™ which are as follows:

- Stage 1 – Heavy metal precipitation;
- Stage 2 - Ettringite precipitation;
- Stage 3 – Carbonation;
- Stage 4 - Recovery of aluminium hydroxide via ettringite decomposition.

SAVMIN™ can recover >95 % of the water, reduce concentrations of trace metals and produce a non-saline effluent stream. The process is run at ambient temperature and pressure hence the electrical power consumption is also limited. However due to the high concentration of calcium sulfate in solution in parts of the circuit, gypsum scaling could be problematic without a proper management plan. The aluminium hydroxide can be recycled where relative costs of the reagents involved, warrant it. SAVMIN™ does not address the monovalent ions, however this should not pose a problem for typical AMD solution compositions as it usually does not contain high concentrations of monovalent ions.

$LoSO_4$™ process

The $LoSO_4$™ process is similar to Savmin but requires large volumes of fresh water in the ettringite destruction stage to avoid solid gypsum formation. If the gypsum were to precipitate, it would contaminate the aluminium hydroxide in the ettringite precipitation stage thereby necessitating the Solid-Solid (S/S) separation step of SAVMIN™. A larger aluminium hydroxide recycle stream would be required if the recycled aluminium hydroxide is contaminated by gypsum. The use of HCl as an alternative means for ettringite destruction also introduces Cl-ions into the product water which complicates the system (Veolia, 2017).

ABC and MBA processes

The energy requirement for the ABC process would be relatively high due to the thermal reduction in the barium sludge processing step which is required for $BaCO_3$ recycling. The MBA process is an enhancement on the ABC process where magnesium hydroxide is also separated as a by-product. Barium carbonate is very toxic and if any unreacted barium carbonate were to pass through to the effluent stream it would have serious consequences (Beer, 2012).

Biological Sulfate Reduction

Mintek BSR

Biological treatment, using sulfate reducing bacteria (SRBs), can be used to purify effluent streams from the mining and metallurgical

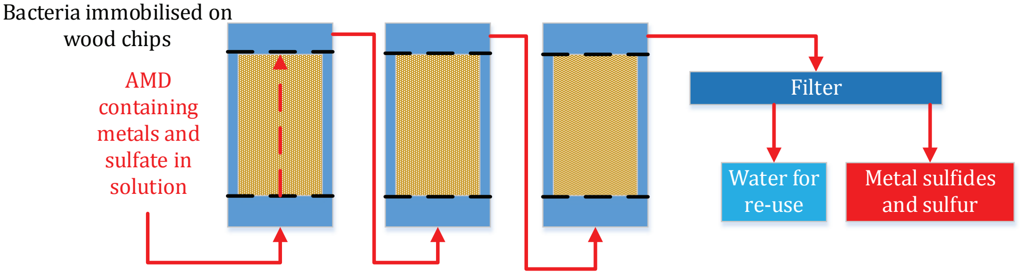

Figure 4: Schematic diagram of BSR process

industries. Biological sulfate reduction can be conducted in both passive and active systems. Passive systems maintain a large working inventory and operate slowly but require low maintenance, low operational input and use natural materials such as woodchips, gravel, manure and compost as substrate. In contrast the active treatment proceeds rapidly hence it requires a smaller inventory but requires frequent human intervention for maintenance and monitoring, requires external sources of chemicals, energy (electrical power) and labour, and incurs higher capital costs for infrastructure development. The active biological method involves the use of bioreactors which have the advantages of being compact and can offer more consistent performance and control while permitting the recovery of metals and sulphur as an added revenue stream to reduce the net operating costs.

Biological treatment of mine effluents and AMD offers a cost-effective and sustainable alternative to conventional treatment technologies. The process uses anaerobic SRB in the presence of organic substrates to remove sulfates and precipitate metals as metal-sulfides, while simultaneously producing alkalinity that raises the effluent pH.

A BSR pilot plant was commissioned at Sibanye-Stillwater, Randfontein on the West Rand of Johannesburg, as shown in Figure 5.

The BSR process removed more than 95% of the sulfates, and the treated water met the stringent South African discharge limits for sulfates (between 200 mg/L and 600 mg/L). The concentration of metals were reduced to trace amounts and the process produced considerably less solid waste, with decreased toxicity and increased stability compared to conventional chemical precipitation methods. The CAPEX is relatively low and the OPEX is reduced when using inexpensive carbon sources and/or a passive or semi-passive treatment design.

Figure 5: BSR pilot plant at Sibanye-Stillwater

Physico-chemical treatment processes

Electrocoagulation

The electrocoagulation system requires regular maintenance. There is the risk of electrode passivation over time which would reduce its efficiency. It is a relatively new technology compared to the typical water treatment processes (such as Reverse Osmosis (RO) and HiPRO) and limited information is available regarding the product water specifications. One of the main deterrents to the technology is the high electrical consumption, which directly impacts on the OPEX.

Membrane technology

Membrane technology cannot treat AMD directly. A pre-neutralisation step is required to remove the bulk of the metals from solution prior to purification. The membranes are prone to scaling and require regular maintenance which adds to the OPEX of the process. The membranes also have a limited lifespan which can further increase the OPEX (ENVIRONMENTAL, LORAX, 2003). The GYP-CIX process can tolerate relatively high concentrations of calcium, however the Total Dissolved Solids (TDS) needs to be less than 4000 mg/L SO_4^{2-}.

HiPRO process

The HiPRO process combines both precipitation and membrane technology. It produces potable water and requires relatively high maintenance of ultrafiltration and reverse osmosis membranes due to scaling. It also results in brine formation which cannot be discharged into rivers. The brine water is thus stored in large lined ponds at a high cost, and would need to be treated at some stage.

Secondary Waste production

Waste stream generation needs to be minimised to ensure that another potential hazard is not created. The amount of waste which is produced for the different processes are compared in Table 2.

Biological sulfate reduction would be the most favourable option as it does not produce a brine and the sludge generation is low to moderate.

Impact of legislative framework

Wastewater treatment plants in South Africa are regulated by the Constitution of the Republic of South Africa, 1996, the National Environmental Management Act 107 of 1998, the Water Services Act 108 of 1997, the National Water Act 36 of 1998, Provincial legislation, Municipal by-laws and other Government policies applicable to Local Government. However this comprehensive framework is applied retrospectively and cannot hold the current owners accountable for damages which were caused by AMD if the previous owners of the mines do not exist anymore. The AMD problem is mainly caused by defunct mines which are ownerless. Presently a comprehensive liability regime is required to prevent this disaster from occurring in the future. With regards to the current damage which was caused by AMD in the case of unidentifiable or non-existent liability, it would be up to the government and the taxpayer to pay for remediation and damages.

Conclusions

When choosing an appropriate AMD treatment technology, the following should be considered:

Table 2. *Waste by-products produced as a result of AMD treatment (Arnold, 2016), (ENVIRONMENTAL, LORAX, 2003)*

Chemical treatment processes with mineral precipitation	Sludge production	Brine production
Chemical treatment processes with mineral precipitation	Moderate-High	No
Biological sulfate reduction	Low-Moderate	No
Physico-chemical treatment processes	Low-moderate	Yes

- Composition of the inlet water;
- Specifications of product water;
- Infrastructure and space available;
- Waste generation.

These factors will identify possible pre-treatment steps required ahead of the chosen technology, and it also needs to be considered in calculating the OPEX and CAPEX of the technologies considered. Of course in general, costs can be expected to increase with increasingly demanding specifications of the product streams. Currently there is no 'silver bullet treatment' option but rather an integration of different solutions depending on the requirements of the product water. Storage/treatment of waste products also should be considered when calculating the OPEX. Secondary waste generation should also be carefully considered to ensure that additional environmental problems are not created. A concerted effort has gone into finding solutions to treat AMD over the last two decades which has resulted in a number of new developments. Progress has definitely been made and each technology is continually evolving to find the most economical and environmentally safe solution.

Acknowledgements

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