

# CURRENT METHODS FOR THE REMEDIATION OF ACID MINE DRAINAGE INCLUDING CONTINUOUS REMOVAL OF METALS FROM WASTEWATER AND MINE DUMP

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## 6.1 INTRODUCTION

One of the most critical issues in mining environment is mine water/dump treatment including total removal of metals. The consequences of untreated mine water/dump on human health, aquatic life, environment, and the various economy sectors are very disastrous. The severity and range of mine water problems including reuse and its effect on the health of the community make it essential to give focused attention to research and development activities in the area of mine water treatment. Mining has been the source of income worldwide over the years and it has been practiced for over a century, leaving more than 6000 tailings dams, 4800 abandoned mine sites, and generating roughly 6 billion tons of mine waste in South Africa (Mengistu et al., 2012). Mining operations contaminate surface and groundwater and cause diseases that could be life threatening upon ingestion (Andrea and John, 2010), and can also end up in the human body through eating or drinking them, or by inhaling dust particles containing them. Several mine wastes/dumps are radioactive, toxic, and carcinogens and their primary health effects occur when consumed in water (Fungaro et al., 2012).

Industrially, the constant demand of these metals cannot be neglected, in spite of their environmental risk. Some of them are used for medicinal purposes, mineral identification, or neutron radiography, steel manufacturer, electron acceptors, as catalysts in goods production, or the petroleum industry. Furthermore, they are used in magnets, phosphors, lamps, superconductors, and optoelectronic applications (Kondo and Kamio, 2002; Padlyak et al., 2006). Considering the above mentioned importance and uses of these metals, their removal and recovery from mine water before discharge and also remediation of drainage around the site in which they have been mined is highly recommended.

Furthermore, the rise in demand for the remediation and removal of metals from mine site is also due to the fact that some of these elements are above their discharge limits into the environment. For instance, uranium concentrations in mine water are usually in the range of 0.01–10  $\mu\text{g L}^{-1}$ , locally up to 500  $\mu\text{g L}^{-1}$ , whereas thorium concentrations usually are below the  $\mu\text{g L}^{-1}$  level. In addition, small

amounts of transuranium elements are continuously formed in nature due to neutron capture in uranium (Allard, 1984).

Acid mine drainage (AMD) remediation can be complicated due to its composition, many researchers have used various techniques such as chemical precipitation, solvent extraction, micellar ultrafiltration, organic and inorganic ion exchange and adsorption (Hobbs et al., 2001; De Marco et al., 2003). The result of high concentrations of metals presence in the water bodies is an indication of the ineffectiveness of some conventional wastewater treatment technology being applied in the mining industry. In this regard, this chapter reviews the achievements and limitations of the above mentioned technologies as well as current methods/technologies in remediating the problems regarding the mine site.

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## 6.2 COMPOSITION OF MINE WATER

Mining operations unlike other sectors are fully reliant on the location of minerals with limited options to mitigate and adapt to regional water or quality impacts (Akinwekomi et al., 2016). Chemical characteristics generated from mine activities with natural water are termed mine water or mine waste drainage. This activity has successfully elevated mining companies across the globe to refine minerals, reduce waste, limit pollution, and drive profitability. Mine water comprises of AMD, neutral mine drainage, and alkaline scarcity mine drainage. When mine and mine waste drainage have neutral pH, with a high concentration of dissolved metals, they are called neutral (or alkaline) mine drainage (Lottermoser, 2010). When the rocks made of sulfur are excavated from a mine surface or an underground mine, they react with water and oxygen to form sulfuric acid. This acid is carried off the mine site by rainwater or surface drainage and gets to the nearby streams, rivers, or lakes; thereby impacting negatively on the quality of this water body. Even though AMD has received greater attention than neutral or alkaline mine drainage, their environmental adverse effects can still not be neglected. In general, mine water comprises of potentially toxic substances that can affect water quality, thus making water pollution a global concern (Wolkersdorfer, 2008).

### 6.2.1 METALS OF SERIOUS CONCERN IN MINE WATER

The majority of economically mine deposits are associated with potentially hazardous trace and harmful elements. The greatest threat posed to water resources arises from mine discharges that have been found to be contaminated with metals, transition metals, and inner transition metals. In the midst of the above mentioned pollutants, iron sulfate, radioactive and rare earth (REEs) metals have been a serious challenge in mine water treatment due to their chemical and physical properties. Sulfate, for instance, is very soluble and this makes its removal a very tedious task (Tolonen et al., 2016). The consumption of drinking water containing sulfate concentrations in excess of  $600 \text{ mg L}^{-1}$  commonly results in laxative effects, therefore the allowable sulfate concentration in drinking water has been reported to be between 250 and  $500 \text{ mg L}^{-1}$  due to its lower environmental risk compare to other dissolved metals (INAP, 2003). This has been under investigation and in many practices; and little or no useful information has been documented. Tolonen et al. (2016)

reported the use of precipitation techniques in sulfate removal and this happens to be the only reliable technology in sulfate removal up till date, therefore more research has to be done. Iron oxide hydride usually present in very high concentration in mine water regardless the type or location of mine site. Precipitation and adsorption are commonly efficiently used in Fe removal but require effective sorbent media and they are termed low-cost technologies. Radioactive and REEs minerals are also a challenge in industrial world owing to their unavailability but can still be found in mine dump; therefore more research is required in the area of their recovery for sufficient supply. Adsorption process can also be sufficiently used to remove trace of radioactive and REEs afterward, provided an efficient sorbent media is applied (Oyewo et al., 2016). Other common metals that can be found in mine effluents are Cd, V, Cu, Al, Cr, Hg, Pb, Zn, Ni, etc.; these can also pose a serious risk to human and aquatic life depending on their bioavailability (Smith and Huycks, 1999).

### 6.3 EXISTING TECHNOLOGIES AND THEIR LIMITATIONS IN METALS REMOVAL FROM MINE WATER/DUMP

There are several technologies used in mine water treatment, and their applications depend on the aims and objectives for the treatment. There are two major categories of AMD treatment options for cleanup of AMD, namely active and passive. The active treatment methods include the application of alkaline chemicals to precipitate metals, and other techniques such as adsorption. Moreover, techniques used efficiently for metal recovery might not be suitable for total removal of metals from mine water or polishing of mine effluent for the purpose of water reuse. Therefore, the technologies for mine water treatment in different categories for different application are summarized in Table 6.1.

**Table 6.1 Mine Water Treatment Options**

Category	Examples	Application
Neutralization	Lime or limestone addition	Acid rock drainage
Passive treatment	Wetland systems	Polishing
Metals removal	Sulfide precipitation, biological filters, fluidized bed reactor	Metal recovery, saleable product
Metals removal	Hydroxide precipitation, coagulation–flocculation, clarification	Metals removal, arsenic removal
Membranes	Microfiltration, ion exchange, reverse osmosis	Water reuse, metals removal
Biological treatment	Fixed film or suspended	Nitrogen, selenium removal, bioleaching
Evaporator and concentrators	Brine concentrators, crystallizers	Zero liquid discharge
Dewatering	Clarifiers, dissolved air floatation	Volume reduction or tailings
Filtration and thickening	Pressure filters, paste thickeners	Volume reduction or tailings
Cyanide treatment	Alkaline chlorination, hydrogen peroxide process	Gold mine effluent

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The outcomes and the limitations of some of these technologies are discussed as follows:

### 6.3.1 REVERSE OSMOSIS IN METALS REMOVAL FROM MINE WATER

Treatment of AMD by reverse osmosis (RO) has been in existence for ages; this technique has the capacity to eradicate contaminants such as bacteria, viruses, and all kind of metals even at trace level, up to 99.8% (Anil et al., 2013). In the course of past decades, membrane technology has been gradually introduced into industrial wastewater treatment. The pressure-driven membrane processes such as RO has found application in mine effluent treatment. RO is semipermeable, dense membrane that is able to reject all dissolved low molecular weight organics and multivalent and monovalent ions (Nidal et al., 2012). Two fluids containing different concentrations of dissolved solids that come in contact with each other will mix until the concentration is uniform. When these two fluids are separated by a semipermeable membrane, the fluid containing the lower concentration will move through the membrane into the fluid containing the higher concentration of dissolved solids (Binnie and Kimber, 2002). Eventually, the water level will be higher on one side of the membrane through the osmotic pressure and the natural osmosis effect must be reversed for the achievement of water purification via RO membrane. To force the water of the brine stream (high-salt concentration) to flow toward the fresh stream (low salt concentration), the water must be pressurized at an operating pressure greater than the osmotic pressure. As a result, the brine side will get more concentrated. The efficiency of this technique is in no doubt, it can even treat mine water up to drinking water requirement (Atkinson, 1997) but the cost of instrumentation, operation, and maintenance is highly expensive and sophisticated (Pisa and Gulikova, 2005)

### 6.3.2 BIOLOGICAL TREATMENT IN METALS REMOVAL FROM MINE WATER

This technique mostly involves the removal of nutrients such as phosphate and nitrate. Biological water treatment involves aerobic, anaerobic, and anoxic process stages, and each stage is for different purposes. Aerobic treatment alone is not viable because the oxidation ponds, as well as high energy consumption for aeration, cooling system are required. Furthermore, anaerobic stage needs no oxygen to operate, whereas anoxic stage can only be operated in the presence of oxygen (Vincenzo and Luigi, 2012). The frequent changes in the diurnal temperatures at each stage make the system performance unpredictable and almost 50% of the COD is converted to sludge after aerobic treatment and this requires secondary treatment (Sennitt, 2005). Fenton oxidation with the prepared coal fly ash/sewage sludge carbon composite as catalyst, and the iron, silicon and aluminum oxides as cocatalytic was reported (Zhang et al., 2016). Meanwhile, heterogeneous Fenton not only significantly improved the effluent quality but also remarkably enhanced anaerobic granular sludge properties that facilitated the high efficiency and ecosystem stability in the bioreactor. Radioactive minerals (Joksic and Katz, 2015) and coal mining effluent treatment using biological treatment and the constraint were also reported (Cravotta and Brady, 2015).

Though the sludge recovered contains chemical surfactants at a considerable concentration ( $60\text{ mg L}^{-1}$ ) depending on the water matrix for industrial reuse, the cost of secondary treatment cannot be neglected (Sailatha et al., 2016). The use of activated sludge treatment, fungi such as *coriolus*, *aspergillus*, and *phanerochaete* and certain bacterial species such as *bacillus*, *alcaligenes*, and *lactobacillus* has been explored in removal of vanadium from industrial wastewaters. However, these methods are inadequate in treating vanadium-contaminated wastewater because vanadium hardly decomposes at the prevailing conditions in the treatment system; therefore, this method was found to be time consuming and has limited performance.

### 6.3.3 CHEMICAL PRECIPITATION TECHNIQUES IN METALS REMOVAL FROM MINE WATER

This process is a conventional technology used in treating mining-influenced water, effluent water, and industrial wastewater. Chemical precipitation processes involve the addition of chemical reagents, followed by the separation of the precipitated solids from the cleaned water. Typically, the separation occurs in a clarifier, although separation by filtration or with ceramic or other membranes is also possible. In an initial screening procedure, ferrous sulfate, ferric chloride, alum, and lime, are chemicals commonly used in the wastewater treatment industry, were tested individually and in combination. This was probably a result of the inability to find the exact precipitation pH and perhaps the difficulty in detecting a colloidal precipitate in a dark solution by visual means. [Amaral et al. \(2016\)](#) reported the use of this technology in sulfate-bearing AMD (coal and metal sulfides) and the separation was done via flotation. The result revealed the maximum removal percentage (80%–82% of the feed content) appears to be limited by the efficiency of the dissolved air flotation process and the chemical equilibrium of the precipitates, which leaves some soluble sulfate in solution. Bubbles readily attach to the flocs and become entrained and/or entrapped in the flocs, creating aerated flocs. Because all of these mechanisms operate simultaneously, the flotation of the flocs is very rapid, as indicated by the high kinetics rate constant. AMD that contains various toxic heavy metals as well as dissolved iron and aluminum that contaminate downstream areas was also treated using this technology and the limitation was also discussed ([Park et al., 2015](#)). [Riodan et al. \(1997\)](#), combined precipitation and biosorption methods using residual brewery yeast as biosorbent media and reported  $360 \text{ mg g}^{-1}$  biosorption capacity, this confirms the efficiency of these methods but not environmentally friendly due to the requirement of large settling tanks for the precipitation of voluminous alkaline sludge therefore, a subsequent treatment is needed.

### 6.3.4 FILTRATION/COAGULATION TECHNIQUES IN METALS REMOVAL FROM MINE WATER

This is a volume reduction technique in mine water treatment, weather tailings filtration and thickening or AMD. It is more of physical technology use for the removal of bigger or smaller particles from wastewater before undergoing any chemical treatment. Coagulation of dirt in mine water always precedes filtration; these processes cannot be efficiently used separately and can be termed two in one process ([Dong et al., 2016](#); [Fu and Wang, 2011](#)). Moreover, this process is also applicable in other mine water pollution control technologies where it is used as a mode of reactants separation. For instance, separation of used adsorbent from solution in adsorption process, and also sludge removal from processed water can be done by filtration or sedimentation. It has been reported that the coagulated sludge serve as media for the removal of some metal(loid)s ([Devi and Saroha, 2017](#)) from mine water such as arsenic removal by iron coagulated and precipitate sludge followed by filtration, this usually happen in iron coagulation ([Pawlak et al., 2010](#)). There are so many coagulants such as alum and lime but alum coagulation is generally less efficient than iron coagulation, so alum should only be used in systems with low arsenic concentrations, which is not the case at the Smith Mine ([Madin, 2007](#)). [Chellam and Clifford \(2002\)](#) also reported the combination of coagulation and membrane filtration techniques for the removal of molybdenum, selenium, uranium, radium, thorium, and other mono- and divalent ions from mine water in a shallow unconfined aquifer influenced by uranium tailings. Iron coagulation process was used and  $10 \text{ mg Fe}_{3+} \text{ L}^{-1}$  dose at pH 4 and 10 was found to be very effective for removing radium and thorium from mine water. Molybdenum and uranium removals by coagulation are

consistent with surface complexation and electrostatic interactions between major coagulant and contaminant complexes in solution. Selenium [Se (VI)] removal was reported inefficient owing to its dominated species in the surficial groundwater.

### 6.3.5 ION EXCHANGE TECHNIQUES IN METAL REMOVAL FROM MINE WATER

Wastewater ion exchange service is a service-based option that utilizes ion exchange resins and other media selected to remove specific ionic contaminants from groundwater, industrial wastewater, and process water for recycle. Pet coke leachate, which is a by-product of petroleum consisting carbon and ash, was used as ion exchange in removal of vanadium. It consists of  $0.06,248 \text{ g L}^{-1}$  anions resin vessels in lead-lag configuration as well as  $0.06248 \text{ g L}^{-1}$  of selective cation resin (Inglezakis et al., 2003). The anion resin targets the vanadium, while the cation removes nickel. Once exhausted, vessels are returned to the processing facility where the contaminants are removed from the media/resin. This process is environmentally friendly and not too expensive to maintain. Anion and cation resins as well as ion exchange membranes are the common ion exchange media in wastewater treatment. It was reported that the rate of resin particle radius was in accordance with the particle diffusion controlled mechanism, and the stirring speed variation does not affect the process rate, which is simply means that process variable has little or no effect on ion exchange controlled mechanism (Miron et al., 2005). Stranska (2015) also reported in a review article the development, characterization and application of ion exchange membranes. The membranes were prepared from polyethylene as matrix, ion exchange resin powder, and polyester fabric using Mohr method; these can be used in different application such as, but not limited to, wastewater treatment. Therefore, the effectiveness of this mechanism cannot be overlooked but due to some disadvantages associated with this method, such as iron fouling, adsorption of organic matter and bacterial contamination, it is regarded as inefficient.

### 6.3.6 ADSORPTION TECHNIQUES IN METAL REMOVAL FROM MINE WATER

Adsorption is mainly surface process, which occurs when a gas or liquid solute gathered on the surface of adsorbent media, forming a molecular or atomic film, while desorption is the opposite of this process. The term sorption comprehends adsorption and absorption processes but they are totally different mechanisms. On the other hand, absorption is a process where by a substance diffuses in to a liquid or solid to form a solution (Macedo et al., 2015).

This advanced technique can be applied for different purposes but quite robust in terms of wastewater treatment effectiveness. It is highly economical, mostly depending on the choice or type of adsorbent used. Adsorbents are usually in the form of moldings, spherical pellets, or rods. Adsorbent must possess high abrasion resistance, to enhance surface capacity for adsorption as a result of higher exposed surface area. They should also possess a distinctive pore structure and diameter, which allows fast transportation of the vapors (Ferrari et al., 2010). This process can be used in mine water treatment for the removal of metals even at trace level; it is highly efficient in very low metals concentration. As mentioned above, the performance of any adsorption process depends on the choice of sorbent media and the most commonly efficiently used is activated carbon (Caccin et al., 2016). Other adsorbents such as polymer-based, zeolite-based, clay-based, and agricultural waste (Frantz et al., 2017; Luisa et al., 2016; Sabirjanovna et al., 2016; Santofimia and

Lopez-Pamo, 2016; Song et al., 2016; Wu et al., 2017) have also been investigated in metals removal from mine water but their limitation is either cost-effectiveness or limited performance, therefore more research is required in the area of effective and efficient sorbent media development.

Kefeni et al. (2017) reported the research article from 1980 to 2016, but lay more emphasis on the latest papers published in between 2010 and 2016 to address up-to-date AMD treatment options. Kefeni and his coworkers revealed that about 200 references are included in the current paper and 79% are those published since 2010. Moreover, each author extensively discussed their prevention and remediation options based on their experience and observation in real AMD issue. The authors believe that their review is very important to design and look for an alternative best technology for prevention of AMD generation including continuous metals removal in the future.

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## 6.4 NOVEL/CURRENT TECHNOLOGIES IN MINE WATER TREATMENT

Improvement of treatment technologies in water pollution control reduces the aforementioned limitations. The development and utilization of specific nanomaterials for mine water, industrial wastewater, bacterial treatment, and novel prototype development are being explored in many academic and industrial institutions (Ray et al., 2012). This innovative use of nanomaterials and prototype development are another potential useful application that needs thorough research. All the above discussed technologies can be upgraded or improved with application of newly developed nanomaterials for different techniques.

### 6.4.1 NEWLY DEVELOPED NANOTECHNOLOGY AND NANOMATERIALS FOR MINE WATER TREATMENT

Nanotechnology has provided innovative solutions for water purification over the years, and its efficiency cannot be neglected. Mokhatab and Islam (2009) reported the positive and negative environmental impacts of nanotechnology and also proposed to understand and characterize these impacts. Though, nanoscale structure is diminutive in size, they are immensely powerful in capacity, the smaller the size, the more the capacity increases. These nanoscale technologies are already being used for enhanced sensing, treatment, and remediation of environmental contaminants. On the bright side, future developments in nanotechnology may lead to greater control over the design of chemical and engineering technologies, such that pollution may be prevented completely. For instance, the development of nanofilters in nanofiltration process has been proven efficient (Momba et al., 2017; Palit, 2017). Novel nanotechnology in mine water treatment up to drinking water was reported by Wang et al. (2016). Furthermore, the use of nanomaterial in mine water treatment has also been investigated by many researchers (Armarego, 2017; Jones et al., 2016; Oyewo et al., 2016; Pal, 2017; Qu et al., 2013; Street et al., 2014; Suthar and Gao, 2017) and reported to be highly efficient in mine water treatment. One of the common drawbacks on many developed nanomaterials is cost-effectiveness. On the other hand, the novel characteristics of nanotechnologies may also lead to unforeseen environmental problems such as new classes of toxins or related environmental hazards, therefore additional researches required to further predict future effects (Balaure et al., 2016; Figoli et al., 2017; Gautam and Chattopadhyaya, 2016; Kunduru et al., 2017).

### 6.4.2 CURRENT MINE WATER TREATMENT PROTOTYPE AND THEIR ACTIVITIES

In some instances, novel and innovative technologies have been adopted with beneficial results and there are several drivers leading to adoption of more advanced treatment technology such as, but not limited to, aforementioned limitations. Furthermore, there is need for mining companies to protect local environments from contamination and maintain a social license to operate. This requires them to declining investments in mining-related projects and increased operational cost in the area of effluent treatment, and this rendered the existing mine more cost-effective to operate. The treatment technology is not commonly employed to enable process reuse, as the nonprecious metal concentration can be effectively managed with additions of noncontaminated intake water, but there is a risk of contaminant retention when large quantities of process water is recirculated, which can lead to scaling, corrosion, and geochemical interference. The application of innovative wastewater treatment technologies is leading to significant benefit in the mining sector, especially in South Africa where several companies are reusing their effluent for potable and nonpotable applications (Freyberg, 2014).

The fact that previous technologies have reported some promising results in mine water treatment, their limitation cannot be neglected therefore, the adoption and investigation of advanced treatment solutions are highly needed. The review in Table 6.2 shows the novel prototype and their activity in mine water treatment from different countries based on their metals of concern.

**Table 6.2 Current Mine Water Treatment Prototype and Their Activities (Habib et al., 1998; Freyberg, 2014)**

Technology Provider	Technology Description	Recent Activity
GE ABMet	Fixed film, packed bed, anoxic bioreactor used for selenium reduction and removal	Contracted by Anglo coal in 2014 to install fluidized bed reactor (FBR) pilot at mine in northern British Columbia
Headworks Bio	Moving bed bioreactor (MBBR) used for reduction and removal of ammonia and sulfates in mining wastewater	Installed MBBR plant at gold mine in northern Saskatchewan, Canada.
Environgen	Fixed film, FBR using sand or activated carbon as the media	The company states having installed 150 FBRs in the United States and has operated two pilot reactors (2011) for coal mining waste treatment
Inotech	Bioreactor uses electrical cells to provide free electrons to microbes, which reduces nutrient dosing requirements. Used for inorganic and heavy metals removal from contaminated streams	Have successful pilot stage demonstration with coal mining wastewater, which shows selenium removal below discharge limit
Frontier water system	Containerized and mobile bioreactor for removal of anions from mining wastewater	No commercial installation to date, bench scale testing has been noted as promised
Virtual curtain	Layered hydroxide/hydrotalcite clay that can adsorb metal ions present in solution may include reverse osmosis (RO) to meet discharge water limit.	Nitrogen, selenium removal, bioleaching

**Table 6.2 Current Mine Water Treatment Prototype and Their Activities (Habib et al., 1998; Freyberg, 2014)—cont'd**

Technology Provider	Technology Description	Recent Activity
Noram engineering	Lignosulfonate-based chemical precipitant for metals removal. Generates a stable sludge by-product that is lower in volume than the high density sludge process.	One pilot plant completed in BC at the Britannia mine site. Potential licensing opportunity as technology is not being utilized.
BioteQ	Biosulphide and chemsulphide processes that use biological and chemical sources of sulfide to selectively remove and recover dissolved metals from mine effluent	Have constructed several chemical sulfide plants most recently, a project in a Chinese copper mine (2011)
Vibratory Shear Enhanced Processing (VSEP) system	The VSEP is used for treatment of mine tailing pond effluent at this facility with no pretreatment required. The VSEP system uses nanofiltration followed by ultrafiltration membrane modules and is able to treat the mine tailing pond effluent, reducing suspended and dissolved solids below the required limits for process recycling or discharge	No recent activity

## 6.5 CONCLUSION

The remediation of AMD is a demanding concept that solely relies on several factors such as the day to day AMD load, net acidity, metal concentration, and flow rate. The outcome and limitation of emerging treatment technologies in mining applications was reviewed and reported. These include biological systems for anion removal, alternative chemicals for metal precipitation, investigations into physical separation technologies for concentrating and recovery process streams, adsorption process, and ion exchange systems used for recovery and metals removal. The novel technologies to remediate these limitations were also reviewed and reported in this chapter. In conclusion, long-term and outstanding research is required for the new developed nanotechnologies and nanomaterials to be widely implemented in AMD affected areas.

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