

Acid mine drainage remediation strategies: A review on migration and source controls

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Abstract

Acid mine drainage (AMD) derives from the oxidation of sulfide minerals, primarily pyrite (FeS_2), and is the most severe environmental issue facing the minerals industry. The most common short-term approach to AMD treatment is migration control, such as acid neutralization and metal/metalloid and sulfate removal, through the addition of alkaline materials, including lime ($\text{Ca}(\text{OH})_2$), limestone (CaCO_3), gangue minerals and industrial wastes. This requires the continuous input of materials and may result in the production of a vast amount of secondary sludge requiring further treatment and disposal. Addition of chemicals is usually more important in metal/metalloid removal than in sulfate removal unless the sulfate is present in very high concentrations. A more promising long-term strategy for AMD prevention is source control through the complete removal of pyritic minerals and encapsulation of potential risk minerals by coating with impermeable surface layers. This is regarded as the most cost-effective approach, although the mechanisms underpinning this and the implementation procedures are yet to be fully elucidated. It is likely that long- and short-term practices can be combined to optimize the remediation of contaminated mining sites. Some factors such as differing geological and mineralogical characteristics and transportation costs must also be considered for the successful implementation of AMD prevention and remediation strategies. This review also considers some implications for AMD remediation, but the promising bioremediation of AMD is not discussed as it has been extensively reviewed.

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Introduction

Acid mine drainage (AMD), also referred to as acid rock drainage (ARD), is a product of the oxidation of sulfide minerals, primarily pyrite, in the presence of bacteria, oxygen and water. It is a widespread environmental problem occurring at both working

and abandoned mining operations. AMD has been identified as the second most serious environmental problem worldwide after global warming, and it is attracting increasing attention (Madzivire et al., 2014; Ríos, Williams and Roberts, 2008). The effects of AMD arising from active mine sites is of less concern compared to their abandoned counterparts due to ac-

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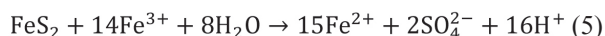
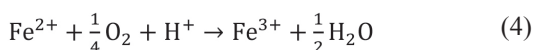
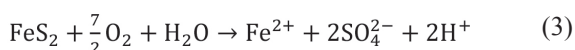
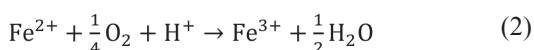
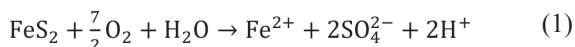
tive pumping resulting in the maintenance of low water tables (Simate and Ndlovu, 2014).

AMD sources and environmental effects. AMD forms in natural environments through a complex interplay of chemical, biological and electrochemical reactions (Parbhakar-Fox and Lottermoser, 2015). Human activities, particularly mining, accelerate this process by significantly increasing the exposure of sulfide minerals to air, water and microorganisms. The majority of currently recognized AMD sources are due to human mining activities (Table 1).

More than 200,000 AMD sites have been identified in the United States alone (Gallinger and Fleury, 2006). Treatment options are currently expensive. For example, Harries (1997) estimated that at operating mine sites in Australia \$120 million per year was required to treat AMD. As the exhaustion of AMD from a given site normally takes decades or even several centuries, the expenditure on remediation strategies worldwide cannot be readily estimated.

AMD effluents are normally strongly acidic and contain high concentrations of dissolved metal/metallloid ions and sulfates that have the potential to contaminate both surface and ground water systems, threatening the health of plants, aquatic and even terrestrial species (Anawar, 2015; Chen et al., 2014; Falayi and Ntuli, 2014; Hatar et al., 2013; Johnson and Hallberg, 2005). Table 2 shows solution assays of some AMD effluents, which vary depending on the mineralogical composition of the mining sites, indicating that the sulfur (S) concentrations of most effluents are significantly greater than the drinking water standard of a maximum level of 250 mg/L, while the heavy metal/metallloid concentrations exceed industrial discharge requirements.

AMD formation. The most common reactions in AMD concern the oxidation of pyrite by air and water (International Network for Acid Prevention, INAP, 2003):



This process is accelerated in the presence of microorganisms (Akcil and Koldas, 2006; Simate and Ndlovu, 2014). The initial oxidation of pyrite occurs through Eq. (1), producing Fe^{2+} , SO_4^{2-} and H^+ , with Fe^{2+} being subsequently oxidized to Fe^{3+} by O_2 in Eq. (2). The kinetics of these two reactions are dependent on temperature, the availability of oxygen (O_2) and water (H_2O), and the activities of microorganisms. Singer and Stumm (1970) reported that the rate-limiting step of pyrite oxidation rate at pH lower than 5 is the oxidation of Fe^{2+} to Fe^{3+} in Eq. (2), which is accelerated 10^6 times by microbes in low pH conditions. The oxidation of pyrite by Fe^{3+} in Eq. (3) only occurs in acidic conditions of pH lower than 3.5, as the solubility of Fe^{3+} is low at neutral or alkaline pH due to precipitation to iron hydroxides or oxyhydroxides in Eqs. (4) and (5).

In addition to pyrite, which is considered to be the primary source of AMD, the exposure of other sulfide minerals, such as chalcopyrite, pyrrhotite and sulfur-containing coal to oxygen and water, also have the potential to produce acid and dissolved heavy metals (Anawar, 2015; INAP, 2003). The acid genera-

tion rates of these minerals are greatly influenced by many factors, including pH, redox potential, temperature, oxygen content, Fe^{3+} activity, bacterial activity and surface area of the exposed minerals (Akcil and Koldas, 2006). Generally, iron sulfides with metal to sulfur molar ratios of less than 1, such as pyrite, marcasite and sulfosalts like enargite, produce acid when reacting with oxygen and water. For sulfides with metal to sulfur molar ratio equal to 1, including sphalerite, galena and chalcopyrite, the production of acidity is not expected when oxygen is the oxidant. However, it should be noted that precipitation of the dissolved metals produces H^+ , resulting in reduced pH in the long term. When aqueous Fe^{3+} acts as the oxidant in the liquid systems, these sulfides are expected to produce acidity (INAP, 2009). However, for sulfides containing S^{2-} , the net acid production is neutral if the source of Fe^{3+} is the oxidation of Fe^{2+} by O_2 , as in Eq. (2), because this reaction removes H^+ from solution to form H_2O . Therefore, the availability and activity of O_2 and Fe^{3+} in the mining wastes play a vital role in AMD evolution.

Note that in addition to oxygen concentration and Fe^{3+} activity, some other factors can also influence acid generation, including pH, temperature and bacterial activity. In other words, AMD can be determined by chemical, physical and biological factors (Akcil and Koldas, 2006). Physical factors such as higher waste rock dump permeability means higher oxygen ingress, contributing to higher chemical and/or biological reaction or reactions.

AMD treatments. AMD treatments have been reviewed extensively (Anawar, 2015; Evangelou and Zhang, 1995; Gazea, Adam and Kontopoulos, 1996; Hengen et al., 2014; INAP, 2003; Lakovleva et al., 2015; Name and Sheridan, 2014; Silva, Lima et al., 2012; Simate and Ndlovu, 2014), including migration and source controls, with the former being divided into active and passive pathways (Johnson and Hallberg, 2005). Table 3 summarizes the advantages and disadvantages of techniques that are potentially and currently used for AMD remediation. Active treatments generally refer to the continuous addition of alkaline materials to neutralize AMD effluents, such as pH adjustment, and to precipitate dissolved metal/metalloids; biological treatment with bioreactors; and other approaches like adsorption, ion exchange and reverse osmosis (Johnson and Hallberg, 2005). The disposal of secondary precipitated sludge, often containing heavy metals, remains a problem, slowing or

Table 1 — AMD primary and secondary sources (Akcil and Koldas, 2006).

Primary sources	Secondary sources
Mine rock dumps.	Treatment sludge ponds.
Tailings.	Rock cuts.
Underground and openpit mines.	Concentrated load-out.
Pumped/nature discharged underground water.	Stockpiles.
Diffuse seeps from replaced overburden in rehabilitated area.	Concentrate spills along roads.
Construction rock used in roads and dams.	Emergency ponds.

Table 2 – AMD effluent assays from selected mining sites. (^aSud et al., 2008; ^bBowell, 2004; ^cGusek and Plocus, 2015)

	Site	Country	Concentration of element (mg/L)																	pH	E_h (mV, SHE)	Conductivity (mS/cm)	References
			Al	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn	Na	Ni	Pb	S	Se	Si	Zn		
Permissible limits for industrial discharge in India	IPB	Spain	100	0.45	300	0.43	—	—	2.2	300	—	2	300	—	—	0.81	—	1300	—	—	—	3.6	—
	Lev-el 500	Finland	—	—	—	—	—	—	76	3400	—	—	—	—	—	1.7	—	—	—	—	—	2.3	—
	Lev-el 270	—	—	—	—	—	—	—	108	911	—	—	—	—	—	13	—	—	—	—	—	2.6	—
	Friendship Hill	United States	56	—	—	—	—	—	—	167	—	—	—	9.8	—	—	—	2200	—	—	—	2.9	—
	Berkeley Pit	United States	—	—	490	—	—	—	186	1100	—	—	420	182	70	—	—	8000	—	—	550	—	—
	WRSA	Canada	177	0.03	194	1.6	1.2	—	3.3	55	—	7	111	12	19	1.1	—	2080	—	—	42	2.7	—
	AMDK	South Africa	45	—	170	—	—	—	—	34	—	—	66	10	41	—	—	1400	—	—	1.3	2.93	415
	Well C	Canada	—	—	587	—	—	—	—	874	—	5.92	575	179	82	—	—	2634	—	—	—	5.82	—
	Königsstein	Germany	—	0.05	300	0.1	—	—	—	120	—	—	—	—	—	0.5	0.5	1500	—	—	15	2.8	3
	Leviathan Mine	United States	107.8	3.2	—	26	—	341	2.2	456.4	—	—	—	—	—	2.56	6.2	—	16.6	—	538	—	—
	DA-8	—	0.08	—	252	0.2	—	—	0.1	0.3	—	14	380	4	114	—	—	2896	—	8	—	3.4	1.87
	Pileta	Mexico	9	—	310	2	—	—	2	178	—	19	1601	26	354	—	—	10118	—	17	363	2.5	4.72
	DA-6	—	41	—	438	6	—	—	12	563	—	21	1759	41	228	—	—	18732	—	35	483	2.4	11.31
	Tailing	—	53373	100	—	—	70	—	98	40103	0.9	—	—	662	—	—	84	3289	—	—	180	—	—
	CW	South Africa	13926	29	—	—	23	—	41	28571	0.1	—	—	284	—	—	22	1176	—	—	29	5.8	5.1
	NW1	—	15913	34	—	—	23	—	32	33301	0.3	—	—	5,486	—	—	65	1070	—	—	67	6.4	4.1
Ahmaruzzaman (2011)	Pérez-López et al.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Lakovleva et al. (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hammarstrom et al. (2003)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Robertson et al. (1994)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kirchner and Mattson (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Castillo et al. (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hardy and Morton (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kassahun et al. (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pascual and McPhee (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Santos et al. (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Lusilao-Makiese et al. (2015)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

impeding the implementation of these methods amid increasingly stringent economic and environmental requirements. Passive treatments, often involving the application of natural and constructed wetlands, normally entail lower construction and maintenance costs than their active counterparts (Buzzi et al., 2013; Sheoran and Sheoran, 2006).

The utilization of nonvalue materials or even those considered to be industrial wastes in AMD treatments has attracted much attention. Ahmaruzzaman (2011) reviewed the application of some low-cost industrial wastes for the removal of heavy metals from wastewater, primarily by adsorption. However, the treatments of AMD effluents by those materials and the related mechanisms are not yet adequately understood.

Although recently published research articles and review papers have proposed various strategies, including both active and passive technologies, to tackle AMD issues, rarely is research published on how to prevent the formation of AMD

at source. The prevention of AMD formation at source is considered the preferred option to migration control of AMD, which is the most commonly used approach for AMD mitigation. However, complete implementation methodologies have not been developed due to incomplete understanding of the remediation mechanism or mechanisms (Johnson and Hallberg, 2005). This area therefore requires more study to improve this strategy to prevent AMD formation, thereby achieving a sustainable pathway.

The aim of this paper is to review AMD treatments currently applied on either the laboratory or industrial scale using limestone, industrial wastes and unvalued gangue or organic materials. When comparing the management practices, we highlight the most sustainable strategy for AMD remediation and prevention during migration and control at source, and focus on the geochemical processes combined with the formation of passivating layers on the acid-producing mineral surfaces.

Table 3 — Summary of AMD remediation strategies (microbial pathways not included).

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Strategy	Materials	Principles	Advantages	Disadvantages	References	
Migration control	Active	Lime and/or limestone	Neutralization	Cheap and easy operation, removal of both heavy metals and sulfate.	High volume of secondary sludge, declined neutralizing capacity due to coating.	Skousen et al. (1990)
		Slag	Neutralization	Fast neutralization, reuse of waste.	Progressively declined neutralizing capacity.	Goetz and Riefler (2014)
		Red mud	Neutralization, adsorption	High neutralizing capability, reuse of waste.	High transportation cost, need care to dispose of the neutralized sludge.	Doye and Duchesne (2003); Tuazon and Corder (2008)
		Fly ash	Neutralization	High neutralizing capability, reuse of waste.	Need care to dispose of the neutralized sludge.	Sahoo et al. (2013)
		Zeolite, attapulgite	Adsorption, neutralization	High selectivity for heavy metals.	Cannot remove sulfate, not reusable.	Falayi and Ntuli (2014); Wingenfelder et al. (2005)
		Isothiazolinone (Kathon RH 886)	Kill bacteria	Reduce bacterial activity quickly, slow down acid-forming rates rapidly.	Short-term control, repeated application required, high toxicity.	Sand et al. (2007)
Source control	Passive	Limestone drains	Neutralization	Little maintenance/cost.	Not suitable for AMD containing high Fe ³⁺ and/or Al ³⁺ .	Cravotta III and Trahan (1999); Johnson and Hallberg (2005)
		Blending of lime and/or limestone	Neutralization	Cost-effective short-term control for AMD.	Long-term remediation effect needs further investigation.	Miller et al. (2009)
		Separating O ₂ /H ₂ O and sulfides	Low cost, easy operation	Not available in all mining sites, seasonal care is required.	Gomo and Vermeulen (2014); Johnson and Hallberg (2005)	—
		Neutralization and coating	Use nonvaluable gangue minerals, potential long-term AMD remediation	Not available in all mining sites, coating layer may not be stable at low pH.	Blowes et al. (2003); Vandiviere and Evangelou (1998)	—

AMD migration control

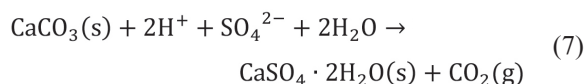
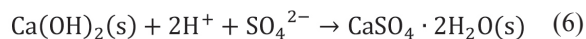
As indicated in Table 3, AMD migration control includes acid neutralization and, where required, the removal of sulfate and toxic metal/metalloids. Heavy metal/metalloids are nondegradable and accumulate in humans to cause severe health problems, while sulfate is less hazardous and nontoxic to humans except at very high concentrations. However, sulfate can impart taste and odor to water at low concentrations, can cause digestive disorders and has laxative effects at concentrations greater than 600 mg/L (Silva, Lima et al., 2012). Howell (2004) summarized the maximum sulfate concentrations permitted in various countries and the World Health Organization recommendations, with the lowest maximum levels for effluent and drinking water being 500 and 250 mg/L, respectively, both significantly less than the sulfate concentrations of AMD effluents, which are normally greater than several thousand milligrams per liter (Nancucheo and Barrie Johnson, 2014; Neculita, Zagury and Bussière, 2008; Song et al., 2012).

Apart from the microbial processing of AMD, such as by using wetlands or bioreactors, the most common technology for AMD migration treatment is precipitation resulting from the addition of alkaline materials, including lime or limestone, slag, bauxite residue or fly ash, although this avenue needs the consecutive addition of the materials and can result in the production of huge volumes of secondary sludge (Wingenfelder et al., 2005). Most heavy metal/metalloids can be removed by raising the AMD solution pH using alkaline materials, as the solubilities of metal/metalloids are normally reduced at higher pH. Nevertheless, the removal of manganese is not readily achieved by the addition of lime or limestone, as a pH of 11 is required for the effective removal of manganese as hydroxide (Ellis, Bouchard and Lantagne, 2000). Zinc removal can also be problematic, requiring a pH greater than 8 (Gupta and Mukherjee, 1990). Recently, both manganese and zinc hydroxide precipitation have been observed to occur at lower-than-expected bulk pH of about 6 to 10 and 6 to 7.5, respectively, possibly due to nonhomogeneous precipitation. However, either these pH conditions must be maintained to stop redissolution of the precipitated phases, or the phases must be separated from the effluent water, or they must be stabilized by subsequent chemical reaction to insoluble phases (Carranza et al., 2016). Silva, Cunha et al. (2012) reported that a combination of limestone and sodium carbonate is beneficial to manganese removal from AMD. Other techniques such as membranes and ion exchange are also recommended for the removal of dissolved metal/metalloids and sulfate (Akcil and Koldas, 2006; Howell, 2004; INAP, 2003; Johnson and Hallberg, 2005). However, these are not well utilized, primarily due to high operating costs compared to using lime and limestone or other nonvaluable minerals or even gangues.

AMD remediation using lime and limestone. Although huge amounts of lime and limestone, which are considered “resources” and not “residue” (Li et al., 2015), need to be added, the practice of adding lime and limestone is most commonly used for AMD treatment in mining sites to neutralize acidic solution and precipitate heavy metals and sulfate. However, this approach is not sustainable in the long term, either financially or from a resource availability perspective.

Most heavy metals can be removed by adding lime and/or limestone, and sulfate can be precipitated as gypsum. The addition of Ba^{2+} to produce barium sulfate precipitation or Al^{3+} to precipitate ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) to remove sulfate has also been reported (Benatti, Tavares and Lenzi, 2009; Silva, Lima et al., 2012). Liming, resulting in

gypsum crystallization, has been reported as a cost-effective process for the bulk removal of sulfate from AMD with high sulfate concentration (Tait et al., 2009) due to its availability and low cost in many countries (Hammarstrom, Sibrell and Belkin, 2003). The reactions for sulfate removal by lime and limestone addition, respectively, are:



The extent of sulfate removal is determined by the solubility of the gypsum, which in turn is dependent on the composition and ionic strength of the solution (INAP, 2003). Therefore, the addition of lime or limestone is recommended as the first step to treat high-sulfate AMD (Geldenhuis, Maree and de Beer, 2003), reducing the sulfate concentration of AMD to less than 1,200 mg/L (Glombitza, 2001).

However, limestone normally becomes covered by the precipitation of iron and aluminum, lowering its activity or even causing it to fail as an AMD treatment. Due to its slow dissolution rate and potential coating by metal hydroxides, limestone is not recommended for waste rock sites with acidity greater than 50 mg/L as calcium carbonate (CaCO_3), or iron concentration greater than 5 mg/L (Skousen et al., 1990). However, introducing carbon dioxide into AMD to increase the limestone dissolution rate, in addition to applying pulsed fluidized beds to scour the coated limestone surface, has been successfully applied in field tests at several sites with moderate acidity of 300 mg/L as CaCO_3 and iron concentration of 30 mg/L (Sibrell et al., 2000). Subsequent study has indicated that this technology can treat AMD from an inactive coal mine in Pennsylvania with acidity of 1,000 mg/L as CaCO_3 and iron concentration of 150 mg/L (Hammarstrom et al., 2003). This method may also add carbonic acid, however, which must then be treated in a later process.

In order to improve the application of limestone for AMD migration control, modification of the limestone surface has been suggested. For instance, Lakovleva et al. (2015) used salt (NaCl) and mining process water to modify the surfaces of limestone to treat AMD water and found that the modified limestones were capable of removing Cu^{2+} , Fe^{2+} , Zn^{2+} and Ni^{2+} . Moreover, the removal of cations was not only due to precipitation by adding alkaline materials such as limestone, but also may be ascribed to the adsorption of formed poorly crystalline materials like ferric hydroxides due to precipitation (McDonald, Webb and Taylor, 2006).

AMD remediation using industrial byproduct wastes.

Slags. Slags are a primary byproduct of the industrial smelting of metals such as steel and copper. They have highly alkaline properties due to the presence of hydrated amorphous silica, calcium oxide and magnesium oxide. In particular, steel slag contains high surface concentrations of readily dissolvable alkalinity (Ziemkiewicz, 1998), mainly $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{Fe})$ -silicates (Huijgen and Comans, 2005). Steel slag has been added to acidic soil for many years as an effective pH modifier (Munn, 2005). Adding steel slag to AMD increases the solution pH and removes heavy metals rapidly, providing an alternative strategy for AMD treatment (Bowden et al., 2006; Kruse et al., 2012; Name and Sheridan, 2014).

Goetz and Riefler (2014) investigated the potential use of steel slag leach beds for AMD neutralization and found the initial alkalinity of approximately 1,500 mg of CaCO_3 per liter

derived from steel slag to be promising. However, a significant decline in neutralization capability was observed in a later stage primarily due to the thickness of precipitation layers being increased on both the slag and the effluent pipe, resulting in low flow rate and, subsequently, low alkalinity loading, and the reduced amount of soluble calcium compounds on the slag surface also contributing to the decreased alkalinity loading.

Name and Sheridan (2014) found that basic oxygen furnace slag also presented a promising alternative to lime. Adding the slag raised AMD pH from 2.5 to 12.1 and removed 99.7 percent of the sulfate (5,000 mg/L) and 75 percent of the iron (1,000 mg/L) within 30 min.

Bauxite residue. Bauxite residue, or red mud, is a byproduct of alumina refining, primarily from the Bayer process. It is usually considered a solid waste of great environmental concern due to its high alkalinity and fine particle size (Liu, Naidu and Ming, 2011). At least 2.7 Gt of bauxite residue worldwide have been disposed in landfills or in open areas, leading to significant regulatory and community concerns. Given such concerns, various reutilization strategies have been investigated, including construction, adsorbent, soil amendment and recovery of metals (Klauber, Gräfe and Power, 2011). Recently, much attention has been paid to recycling red mud as an effective alternative to lime to neutralize AMD (Paradis et al., 2007; Tuazon and Corder, 2008). Hydroxide, carbonate, aluminate and other buffers contained in red mud suggest it to be an ideal material for acid neutralization, while the large specific surface area of the insoluble metal oxide in red mud provides excellent adsorbent properties (Ríos, Williams and Roberts, 2008).

Doye and Duchesne (2003) demonstrated that red mud had good neutralization capacity for treating reactive tailing samples in the short term. Nevertheless, from a long-term viewpoint, 10 percent of untreated red mud was insufficient to maintain neutral pH conditions or keep the metal concentrations below the discharge requirements. In order to improve the long-term alkalinity of red mud for processing AMD, Paradis et al. (2007) modified red mud by adding brine to convert easily soluble alkalinity to less soluble alkalinity, providing a buffering-like neutralization capacity for further tailing treatment. The addition of brine did not influence the short-term neutralization capacity of red mud as the soluble alkalinity remained sufficient. In contrast, the “stored” alkalinity was retained during water flushing to be released slowly for further neutralization. Hanahan et al. (2004) reported the increased acid neutralization capacity of red mud modified by seawater, and López et al. (1998) demonstrated that gypsum-modified red mud was stabilized in solution as aggregates, while Genç-Fuhrman, Mikkelsen and Ledin (2007) reported that acid-activated, Bauxsol-coated sand improved the removal of arsenic and chromium.

Ash. Highly alkaline coal fly ash, an abundant waste material from coal power stations, has been considered as another option for AMD treatment. Madzivire et al. (2010; 2011) reported that sulfate was effectively removed from AMD solution by adding fly ash to raise the pH to above 11. Addition of gypsum seed was used to initiate the precipitation of gypsum from the saturated solution. Amorphous aluminum hydroxide ($\text{Al}(\text{OH})_3$) was then added to precipitate sulfate as ettringite, reducing the sulfate concentration from 1,043 ppm to 213 ppm. Further study (Madzivire et al., 2014) indicated that the treatment of AMD using coal fly ash also displayed the potential to remove radioactive elements, such as uranium and thorium, thereby purifying the water sufficiently to meet drinking standards.

Sahoo et al. (2013) investigated the ability of coal fly ash

to inhibit AMD generation in column leaching from waste containing abundant pyrite. The iron released from pyrite was found to be immediately precipitated due to the higher pH: neutral or alkaline. The iron oxyhydroxide phases formed on the pyrite surface inhibited further oxidation by providing a physical barrier to water flow and oxygen, thus mitigating AMD generation.

The application of wood ash has also attracted much attention. Treatment using wood ash has shown comparable removal capabilities of iron (Fe), arsenic (As), mercury (Hg), chromium (Cr), cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb) and aluminum (Al) and better removal efficiency of manganese (Mn), zinc (Zn), magnesium (Mg) and sulfate ions (SO_4^{2-}) than using calcium hydroxide (Heviánková, Bestová and Kyncl, 2014). In addition, when wood ash was used, the amount of sludge generated was significantly smaller than when calcium hydroxide was used, due to the much higher alkalinity of wood ash.

Others. As alternative materials to the commercial quicklime or hydrated lime that are commonly used for AMD neutralization, slag and ash byproducts can be applied to provide alkalinity to neutralize AMD effluents and remove metal/metalloids. Tolonen et al. (2014) investigated four byproducts from quicklime manufacturing — partly burnt lime stored outdoors; partly burnt lime stored in a silo; kiln dust; and a mixture of partly burnt lime stored outdoors and dolomite — and observed that over 99 percent of Al, As, Cd, Co, Cu, Fe, Mn, Ni and Zn and approximately 60 percent of sulfate from AMD were removed as precipitates. Among the four byproducts, the partly burnt lime stored outdoors and partly burnt lime stored in a silo showed potential to replace quicklime or hydrated lime due to their high metal and sulfate removal capacities and small sludge production.

AMD remediation using low-cost minerals. As lime and/or limestone are not available at every mining site, the uptake of potentially toxic metals, such as Fe, Pb, Cd and Zn, on low-cost or unvalued minerals has been examined as an alternative for the treatment of AMD waters. For example, Wingenfelder et al. (2005) used natural zeolite (clinoptilolite, $(\text{Na}, \text{K}, \text{Ca})_{2-3} \text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12(\text{H}_2\text{O})$) to remove heavy metals from synthetic mine waters due to its high selectivity for metals such as Pb, Cd and Zn. Pb was removed efficiently from both neutral and acidic solutions, whereas the removals of Zn and Cd were influenced by pH and Fe concentration. Ríos, Williams and Roberts (2008) used natural clinker and synthetic zeolites as sorbents to remove heavy metals in AMD generated at a Cu-Pb-Zn deposit at Parys Mountain. Both cation exchange reactions and precipitation of hydroxide species, predominantly Fe species, played a crucial role in treating the AMD through sorption and coprecipitation of the heavy metals. In addition, faujasite was observed to be capable of selective removal of heavy metals in the order of $\text{Fe} > \text{As} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Cr}$ (Ríos, Williams and Roberts, 2008). Cation exchange capacity of lignite to remove heavy metals from AMD has also been observed (Mohan and Chander, 2006).

Raw attapulgite ($(\text{Mg}, \text{Al})_{25}\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4(\text{H}_2\text{O})$) has been successfully used as an adsorbent for heavy metal removal and as an alkaline mineral to neutralize AMD from a gold mine. A hundred percent of Cu^{2+} and Fe^{2+} , 93 percent of Co^{2+} , 95 percent of Ni^{2+} and 66 percent Mn^{2+} were removed at 10 weight/volume percent loading, but the removal rate of sulfate was insufficient (Falayi and Ntuli, 2014). However, once filled up, the attapulgite, as well as zeolite, is no longer capable of

removing cations. Therefore, these materials have a limited life span and require sufficient amounts if treating AMD.

AMD source control

Limestone has been used on a field scale for source control. Limestone amendments, blended and layered or added as covers, conducted at Freeport Indonesia and at the Grasberg Mine in Papua Province, Indonesia, have shown effective control of AMD for nearly 10 years when 25 percent limestone was blended. Nevertheless, for longer-term mitigation of AMD, further factors should be considered, such as the compatibility of size fraction distributions and mixing of the limestone with the waste (Miller et al., 2006).

Compared to the remediation of AMD using alkaline materials such as limestone to remove dissolved cations and sulfate, prevention of the formation of AMD at source has now been recognized as a better option for long-term AMD mitigation. The concept of preventing or minimizing acid formation is to separate the sulfide minerals from oxygen or water or both oxygen and water. The flooding-and-sealing approach for abandoned underground mines, for instance, requires flooding of the mine waste by water (Johnson and Hallberg, 2005). The dissolved oxygen contained in the water at about 8 to 9 mg/L will be consumed by the microorganisms present. Subsequently, dissolution of oxygen in the solution is controlled by mass transfer and diffusion, which is inhibited by sealing the mine. Similarly, some mine tailings with acid-producing potential have been protected by shallow water (Li, Aubé and St-Arnaud, 1997), reducing contact between the minerals and oxygen. This method could be improved by covering the tailings with a layer of organic material or sediment, both of which may limit oxygen ingress. However, these methods are only effective where there is sufficient water, with efficacy reduced by acute wet and dry seasons, especially when drying and cracking of the cover occurs. As AMD is due to the oxidation of sulfide minerals in the presence of oxygen, water and bacteria, the methods reducing their roles can be applied to prevent AMD. According to Pozo-Antonio et al. (2014), AMD can be prevented by techniques such as soil compaction, dry cover, and cover using mining waste, slag and clay minerals. The addition of chemicals to reduce the activity of microorganisms was also recommended.

As sulfide mineral surface coatings have the potential to mitigate AMD, attention has been paid on both the laboratory and field scales to improve and stabilize their formation. For example, Satur et al. (2007) applied an organic *in situ* carrier, catechol, for titanium (Ti) transportation in aqueous environments from Ti-containing minerals to pyrite surfaces to prevent pyrite oxidation. The approach is called carrier-microencapsulation. They confirmed that pyrite oxidation was suppressed due to the formation of a $\text{Ti}(\text{OH})_4$ or TiO_2 layer, resulting in higher pH. However, it would be costly to use Ti-containing minerals as the source for the coating materials.

Evangelou (2001) reported pyrite microencapsulation technologies involving the use of H_4SiO_4 , H_3PO_4 and oxidants of H_2O_2 or hypochlorite, in addition to application of limestone or sodium acetate (NaAc) that maintain pH at neutral to create impermeable phosphate or silicate coatings that can inhibit O_2 or Fe^{3+} ingress, thereby reducing pyrite oxidation. The oxidants were used to produce Fe^{3+} , which further promoted the formation of phosphate or iron silicate precipitates on the pyrite surface. The presence of oxidants is central to this process. Vandiviere and Evangelou (1998) compared conventional — that is, using alkaline materials such as limestone

— and microencapsulation — that is, coating — processes to prevent pyrite oxidation by conducting an outdoor leaching column experiment and found that the silica coating reduced pyrite oxidation most significantly. Scaling up this technique to industrial implementation may be a problem. Zhou et al. (2017) found that acid generation due to pyrite in an acid-forming iron ore waste rock was significantly reduced by the addition of lime and blending of silicates as the top cover in the column. Further strategies to passivate pyrite oxidation have been investigated by Qian et al. (2017).

To date, most of the published studies show the possibility of reducing pyrite oxidation at near neutral pH. Iron oxyhydroxide is formed and developed as a coating on pyrite surface if sufficient alkalinity is available. This layer becomes thicker and denser, further blocking the transfer of oxidants to the under layer of pyrite that then remains unoxidized. Huminicki and Rimstidt (2009) found that iron oxyhydroxide coatings evolved in two stages at near neutral pH. Initially, iron hydroxide colloids were formed in the solution and then attached on the pyrite surface, giving rise to a highly porous and permeable layer. This layer resulted in slightly reduced pyrite oxidation. Subsequently, the interstitial precipitation of iron oxyhydroxide occurred in the pores of this layer, densifying the barrier and thereby suppressing pyrite oxidation by five orders of magnitude.

Kargbo et al. (2004) investigated the effects of a diacylene-containing phospholipid to inhibit pyrite oxidation at pH 2 and 6 in the presence of silicate. At pH 6, both silicate and lipid provided effective barriers, preventing pyrite oxidation and reducing the release of oxidized products, with the latter being better than the former. However, in another study only lipid was found to effectively prevent pyrite oxidation at low pH of 2, with the efficiency decreasing as a function of time. Furthermore, Kargbo and Chatterjee (2005) found that silicate coatings of Fe^{3+} -silica and/or Fe^{3+} -hydroxy-silica complexes on pyrite surfaces resulted in significant suppression of pyrite oxidation down to pH 4, but at pH 2, no silica coating was observed and no passivation of pyrite oxidation was found.

Similar phenomena were observed by Zeng, Schumann and Smart (2013), who added dissolved silicate into an aqueous solution containing pyrite. No reduction in pyrite oxidation was observed at pH < 5.5. However, at pH > 5.5, amorphous iron oxyhydroxide layers were formed and stabilized in the presence of dissolved silicate, forming Si-O-Fe bonds and reducing pyrite oxidation by up to 60 percent. In contrast, in the absence of silicate, crystalline goethite was formed, showing no pyrite oxidation inhibition. It is highly likely that the transformation of ferrihydrite to goethite and/or hematite was impeded by the inclusion of silicate species (Cornell, Giovanoli and Schindler, 1987), which was further confirmed by the recently published work of Fan et al. (2017).

In order to suppress pyrite oxidation at lower pH, such as pH 2.0, Diao et al. (2013) successfully applied silane-based coatings (tetraethylorthosilicate, or TEOS, and *n*-propyltrimethoxysilane, or NPS) to pyrite surfaces to reduce chemical and biological oxidation by 59 and 96 percent, based on Fe release, respectively. This reduction was thought to be primarily due to the formation of a dense network of Fe-O-Si and Si-O-Si bonds on the pyrite surface. The much greater effectiveness of the NPS coating than the TEOS coating was ascribed to the crack-free morphology and the presence of hydrophobic groups on the NPS-based coating surface providing a physical barrier, preventing oxidizing reagents and bacteria from interacting with the pyrite surface.

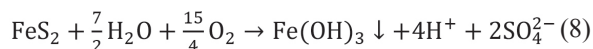
By applying both electrochemical and chemical leaching approaches, Ouyang et al. (2015) found the formation of a

cross-linking network of Si-O-Si and Si-O-Fe covalent bonds formed on pyrite surfaces suppressed pyrite oxidation by 49.4 to 89.2 percent at pH 2. However, they also pointed out that further effort was required to provide a simple coating procedure to form a stable and durable organosilane coating layer on pyrite or tailings minerals in real AMD sites. Miller et al. (2009) reported the evaluation of the long-term performance of limestone blends and covers for AMD control. When remaining at circum-neutral pH, pyrite oxidation was significantly reduced due to the formation of inhibiting surface layers — predominantly jarosite and iron oxyhydroxide — and alumina silicate armours.

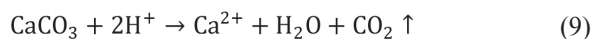
In addition to the coating techniques discussed above, the geochemical processing of AMD using gangue minerals associated with sulfide minerals has attracted much attention recently. The dissolution of carbonates, such as calcite, and noncarbonates, such as chlorite, available at many sites contributes to the neutralization of the acidity generated in the pyrite oxidation process, providing a sustainable and cost-effective strategy in AMD management. Blowes et al. (2003) and INAP (2009) have demonstrated the approach to neutralize AMD and form encapsulation to prevent oxygen attack of the underlying sulfide minerals using carbonate minerals, such as limestone and dolomite.

In the short term, neutralization arising from carbonate minerals slows the oxidation of pyrite and hence the acid generation rate due to the increased pH. Compared to carbonate minerals, silicate minerals are reported to be the most promising gangue minerals for the long-term treatment of AMD, as the rate of neutralization provided by their dissolution can match the acid generation rate after the peak rate of acid generation (Miller et al., 2010). Therefore, investigation of local silicate mineralogy should be undertaken for the low-cost, long-term treatment of AMD. Anawar (2015) briefly reviewed the sustainable rehabilitation strategies for AMD, including geochemistry and mineralogy, and pointed out that the gangue minerals of feldspar, kaolin minerals, aluminosilicates, muscovite, albite, calcite, dolomite, mica and gypsum are always associated with potential acid-forming sulfide minerals such as pyrite, arsenopyrite, pyrrhotite, chalcopyrite, marcasite, galena and sphalerite. The dissolution of these mining wastes is expected to help ameliorate AMD due to their alkaline characteristics.

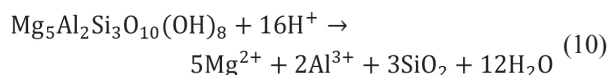
The acid-neutralizing capacity of carbonate and silicates is therefore crucial to determining the extent to which a mine site will produce AMD. For example, the oxidation of 1 mole of pyrite produces 4 moles of protons:



requiring the consumption of 2 moles of calcite:



or 0.25 mole of chlorite:



for neutralization, without considering other reactions such as precipitation due to cation hydrolysis.

For the acidity to be neutralized, the rates of acid generation and neutralization must match. For instance, if the dissolution rate of chlorite is significantly slower than the acid generation rate due to pyrite oxidation, acid will be produced, even if the amount of chlorite is theoretically sufficient.

The effective starting point for geochemical assessment is therefore to comprehensively identify the potential acid-forming and neutralizing mineralogy on site: for example,

Table 4 — Acid-neutralizing rates, noncarbonate (ANR_{nc}), calculated from silicates at four waste sites (Li et al., 2015) (NE = no ANR_{nc} expected).

Mineral	ANR_{nc} (mg of H_2SO_4 /kg/week)			
	Site A	Site B	Site C	Site D
	pH 2.7	pH 3.4	pH 2.9	pH 4.2
Quartz (SiO_2)	NE	NE	NE	NE
Biotite ($\text{KMg}_{1.5}\text{Fe}_{1.5}\text{AlSi}_3\text{O}_{10}(\text{OH})_2$)	123	—	—	—
Clinocllore# ($\text{Mg}_{3.6}\text{Fe}_{1.4}\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$)	—	193	382	71
Albite ($\text{NaAlSi}_3\text{O}_8$)	12	66	—	—
Muscovite ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$)	1	5	4	0.5
Sanadine (KAlSi_3O_8)	6	—	—	—
Orthoclase (KAlSi_3O_8)	—	—	48	—
Total	141	264	434	71.5

the amounts and dissolution rates of nonvalue minerals such as carbonates and reactive silicates that have the potential to treat AMD. The dissolution rates of these neutralizing minerals should be comparable to the acid generation rates due to the oxidation of sulfide minerals. In some cases, if the available carbonates or reactive silicates are insufficient, additional alkaline amendment, such as limestone, may be required to achieve effective mitigation. Detailed investigation regarding the dissolution rates and the available amounts of the primary acid-forming and acid-neutralizing minerals should therefore be conducted prior to any industrial implementation. Once the short-term neutralization capacity derived from carbonate minerals is consumed, the net acid released from the acid-forming minerals could be neutralized in the long term by the gangue silicate minerals (Miller et al., 2010). If the acid neutralization rate matches the acid generation rate, the AMD issue can be regarded as mitigated until all the silicates are exhausted.

The neutralization capacity of carbonates in AMD treatment was reported by Jambor et al. (2002). Detailed information on how to estimate the acid generation and neutralization capacities of wastes by acid-base accounting (ABA) static test methods, including net acid production potential (NAPP), paste pH and single addition net acid generation (NAG), have been well documented (INAP, 2009; Smart et al., 2002). However, these tests only assess the overall net acid-forming/neutralizing potential, not the kinetic rates, and each test has its advantages and disadvantages. Hence, Li et al. (2015) subsequently discussed how to accurately estimate the acid-neutralizing rates of some silicates (Table 4), demonstrating that the dissolution rates vary depending on silicate type and conditions such as pH.

As discussed above, the formation and maintenance of a silicate-stabilized iron oxyhydroxide coating on the acid-forming sulfide surfaces contributes to AMD mitigation by preventing the ingress of O_2 and other oxidants, including Fe^{3+} , to the pyrite. However, the silicate-stabilized iron oxyhydroxide coating is only effective in reducing acid generation at circum-neutral pH, not at more acidic pH conditions, such as pH 3 or 5 (Zeng, Schumann and Smart, 2013). In order to

successfully reduce overall acid generation rates at mine sites, it is necessary to maintain neutral pH in conjunction with a considerable thickness of passivation layers, offering a strong resistance to seasonal changes. Hence, several aspects of the formation of these layers need to be understood: (1) how to maintain the system at a neutral pH if required, (2) how to stabilize the coating layers on the reactive sulfide mineral surfaces at low pH if pH is expected to decline, and (3) how to design and control the geochemical treatment of AMD in a cost-effective way. These issues could be addressed once the stabilization and destabilization mechanisms of these layers are fully understood.

The development of a successful geochemical treatment pathway should consider the widespread minerals that have potential AMD mitigation capacities at sites with current or potential AMD issues. Note that silicates are the most abundant minerals on Earth and are available in most mining sites with AMD issues. They can be regarded as the potential “terminator” for building up a passivating multi-layer to reduce the acid generation rate, eventually providing a long-term on-site AMD mitigation strategy. The precipitated materials may also cover the silicate mineral surfaces, thereby reducing their neutralization effects. This should be considered in the layering process of the silicates in the AMD remediating process following the geochemical manner.

If both carbonates and silicates are available, carbonates tend to be exhausted earlier due to faster reaction between carbonates and acid solution. However, the amount of silicates present in mining sites is not sufficient to ensure perfect AMD remediation. The arrangement and distribution of silicates and AMD-producing source minerals should be a vital factor influencing the remediation efficiency.

Factors in determining AMD remediation strategies

AMD remediation strategies are influenced by a vast number of realities, including environmental regulations, economic and technical conditions, and social factors. It is normally recognized that passive AMD treatments have lower environmental impact than active treatments, predominantly due to the successive additions of chemical and energy input required for the latter. Therefore, a comprehensive evaluation life cycle assessment (LCA) of their net environmental impacts should be considered (Hengen et al., 2014). A sustainability audit of the various AMD treatments can be evaluated by LCA, which therefore can assist in determining the long-term influence of each option. For instance, chemical neutralization of AMD and the precipitation of dissolved metals in the effluents by application of alkaline industrial byproducts is likely to be relatively benign, as it conforms to the “wastes treat wastes” model. Nevertheless, the consumption of fossil fuel to transport the byproducts from the industrial sites to AMD sites should be considered. Normally, mining sites are at locations remote from the source of the alkaline byproducts. Tuazon and Corder (2008) compared the net energy use, fuel consumption and emission levels of carbon dioxide using traditional lime, and seawater-neutralized red mud for treating AMD. The results showed that the seawater-treated red mud generated 20 percent of the carbon dioxide emission and required 44 percent of the electricity relative to lime. However, the fuel usage for implementation of seawater-neutralized red mud was more than 12 times greater than that for lime due to the greater costs of transportation.

In addition, the amount of the materials required for AMD

treatment should be critically examined. As existing AMD sites cover a large land area, and the large volume of discharged effluent influences both the underground and surface water systems, a sufficient supply of these amendment materials is necessary for long-term management. Moreover, the impurities in the industrial wastes used for AMD migration control should be considered. Otherwise, the toxic ions or species might be released into the AMD environment, resulting in serious secondary contamination.

The sustainable strategy in AMD control is source control rather than migration control, as the operational cost of the latter will be significantly greater than the former once AMD commences. Source control combined with microbiological approaches (Johnson and Hallberg, 2005; Simate and Ndlovu, 2014) is likely to be one of the best strategies to consider in terms of preventative AMD treatment. Note that the cost of AMD treatment using various techniques or materials can be estimated using AMDTreat (Office of Surface Mining Reclamation and Enforcement, 2015).

Bioremediation is not discussed in this work due to the extensive discussion reported previously by DiLoreto, Weber and Weisener (2016), Martins et al. (2011, 2010), McCullough and Lund (2011) and Sheoran, Sheoran and Choudhary (2010).

Conclusions and implications

Although the chemistry of AMD generation is straightforward, the final product is a function of local geology, geochemistry, microbiology, hydrology and climate. The combination of these factors results in highly variable AMD generation. Hence, many factors should be considered in designing and implementing sustainable and cost-effective treatments for remediation of AMD. However, prevention and remediation strategies share the same mechanisms: identifying the potential acid-forming minerals and reducing acid formation rates.

AMD neutralization using alkaline materials including lime, limestone, chemicals, gangue minerals, industrial wastes and other materials is the simplest short-term methodology for AMD remediation, but it needs continuous inputs and results in large volumes of secondary sludge that require further treatment. The addition of lime and/or limestone is selected preferably by some mining sites due to low cost of local resources, but often can only reduce sulfate to a concentration that is greater than the discharge standard. This practice is therefore regarded as an option for the first-stage treatment of AMD with high concentrations of heavy metals and sulfates. Although the migration controls for AMD described here are effective, a combination of some technologies is beneficial for the effective, complete removal of sulfate and heavy metal/metalloids.

Source control using low-cost gangue minerals or industrial wastes is the ultimate aim for AMD remediation to achieve zero-waste discharge, on the basis that “prevention is better than cure.” However, various attempts to prevent AMD at source have not been successfully implemented on an industrial scale due to mechanisms that are not yet fully understood and nonoptimal implementation procedures. Short-term neutralization prior to long-term source control treatments may be considered. The latter frequently includes the formation of an impermeable layer on the pyritic mineral surface and requires circum-neutral pH. Note that Si-stabilized iron oxyhydroxide pyrite surface coatings are effective but need further investigation to optimize their formation and stability over a greater range of conditions. In addition, the coating process can be investigated using molecular modeling strategies, which will significantly improve the understanding

of the coating mechanism or mechanisms.

Although the use of low-cost industrial wastes or nonvalue gangue minerals has potential for AMD mitigation, further modification by physical or chemical treatments to increase their adsorptive/neutralizing capacities should be considered. In addition, the toxicity of the metal/metalloids or elements that may be leached out from these materials into the treated AMD during the process of pH raising should be taken into account. If gangue minerals are expected to mitigate AMD, the accurate determination of the ANR of the mineral candidates, such as specific silicates, should also be well understood. Therefore, the development of accurate predictive capabilities for acid generation and acid neutralization rate will be beneficial for long-term AMD remediation.

Climatic conditions — seasonal temperatures, evaporation and rainfall — should also be considered for AMD treatments, as the long-term stability of the pyritic coatings and waste rock dumps covers may be influenced by extreme weather events. Although biotreatment has not been discussed here, the influence of indigenous microorganisms living locally at the AMD sites should be sufficiently considered, as the activity of microorganisms definitely affects AMD formation, the oxidation and dissolution of sulfide and gangue minerals, and the passivation layer-forming process.

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