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Chapter

Sustainable Treatment of Acidic and Alkaline Leachates from Mining and Industrial Activities: Current Practice and Future Perspectives

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Abstract

Water resources are under continued pressure from anthropogenic sources, including acidic waste from abandoned mine sites and alkaline waste from a variety of industrial activities. Large quantities of mine and industrial wastes are typically stored in tailings facilities which can generate significant quantities of leachates due to weathering. If released untreated to the aquatic environment these have the potential to contaminate surface and ground waters. In addition, generation of leachates from abandoned or closed sites presents a major long-term environmental challenge where the generation of leachates is expected to continue for decades if not centuries post closure. An overview of leachate production and associated treatment technologies are described, with an emphasis on passive and potentially sustainable technologies. Measures to prevent the formation of acidic leachates and the potential for resource recovery from acidic and alkaline wastes and leachates are also discussed. Finally, technologies that require further development for long term and sustainable treatment are highlighted.

Keywords: mine and industrial wastes, acid mine drainage, alkaline leachates, passive treatment, resource recovery, sustainability, circular economy

1. Introduction

The mining industry generates in excess of 6 billion tonnes of waste annually [1] with significant growth expected in the future. In the EU for example, annual mine waste comprised 26.3% (615 Mt) of the total waste generated in 2018 [2]. Mine waste is generally categorized as i) non-mineralized overburden (typically 2–20 cm diameter), which is removed to access valuable mine ores and stored in spoil heaps, and ii) tailings and process wastewater, arising from the extraction and processing of ores. Tailings from metal mining are enriched with heavy metals (metals with a density $> 6 \, g \, cm^{-3}$),

whose extraction is no longer economically viable and are typically deposited indefinitely in storage lagoons, often referred to as tailings storage facilities. These storage facilities generate vast quantities of metal rich leachates, which if released to the aquatic environment, can result in elevated bioavailable metal concentrations and sediment loading leading to the stress and death of aquatic organisms and human health.

Leachates are often classified as acidic, alkaline or neutral depending on the geochemistry of the mine tailings and the processing steps utilized in the mining process. Acidic leachates and acid mine drainage (AMD) have a low pH (typically pH < 6) and are generated when sulfidic ores, most commonly pyrite ores (FeS_2, often referred to as 'fool's gold'), which are normally stable in anaerobic underground conditions are exposed to oxygenated environments during mining operations causing the sulfides to oxidize. This process results in acidic conditions (sulfuric acid generated) with associated elevated levels of sulfate, heavy metals and metalloids (semi metals having metallic and non-metallic properties), which if released to the environment result in significant and long-term pollution. The most abundant and common metal in AMD is Fe(II) which reacts with dissolved oxygen to produce iron oxide precipitates. Alkaline leachates on the other hand have a high pH (typically pH > 10) and are generated at disposal sites of industrial by-products such as steel slag, coal ash, municipal waste incinerator ash and bauxite residue from the alumina processing industry. The high alkalinity of these leachates is typically generated from reagents used in industrial processes, such as sodium hydroxide (NaOH) and lime (CaO), and are often enriched with trace metals such as chromium (Cr), vanadium (V), molybdenum (Mo) and gallium (Ga). Neutral leachates (typically pH 6–10) are normally generated from mine wastes low in sulfides or when the oxidation of sulfides is weak or when waste is neutralized by carbonate content in the material [3]. Although neutral, these leachates can contain potentially toxic elements such as water-soluble forms of nickel (Ni), zinc (Zn), cobalt (Co), arsenic (As) and antimony (Sb).

An estimated 3.5 billion tonnes of bauxite residue, a byproduct of alumina refining and more commonly known as red mud, are deposited globally and this amount is increasing at rates of between 120 and 150 Mt. per annum. While it is difficult to accurately predict alkaline leachate quantities generated from these deposits, a global estimate is in the region of 150 million m^3 per annum [4]. These leachates can contain elevated concentrations of metals such as aluminum (Al), potassium (K), sodium (Na), V, Mo, Ga and Ni, which are potentially toxic if released untreated to the aquatic environment. In addition to this, an estimated 30–40 Mt. of incinerated bottom ash and 2–6 Mt. of fly ash are generated annually from incineration of municipal solid waste (MSW). Most of these residues are generated in the EU (33%), China (29%), Japan (20%) and the USA (16%). Despite the varied, significant and potentially valuable metal content of these ashes, most are deposited to landfill with associated generation of metal rich alkaline leachate production [4].

As well as posing a serious threat to the environment and to human health, billions of euros worth of valuable metals contained in industrial and domestic wastes are disposed of in hazardous waste disposal sites [4]. However, metal recovery from these wastes and associated leachates is for the most part technically difficult, uneconomical and unsustainable, primarily because the metals tend to be present in low concentrations and in complex matrices. Nevertheless, resource recovery must remain a priority, particularly in an age where technological advancement is a key driver for global sustainability.

The following sections will examine current treatment options with a focus on passive treatment of acid mine leachates and alkaline industrial leachates. An overview of recent attempts at resource recovery from these leachates will also be discussed before considering future requirements for treatment of acidic and alkaline leachates.

2. Treatment of acid mine leachates

Source control techniques to prevent the formation of AMD is an ideal scenario for the mining industry, which would significantly reduce the environmental burden from mining operations. Source control operates by limiting the exposure of sulfidic waste to air, water or oxidizing bacteria (e.g. sulfide reducing or iron oxidizing bacteria) thereby preventing or reducing its acidification. The most common source control treatments include underwater storage of mine tailings or dry covering with non-reactive materials (oxygen barrier), co-disposal with acid consuming or alkaline producing materials, microencapsulation and passivation. Microencapsulation involves forming an iron hydroxide coating on the surface of the pyrite to inhibit pyrite oxidation and reduce the formation of AMD while addition of a passivation agent facilitates a series of reactions to form a dense inert layer on the surface of the metal sulfide materials which reduces contact with oxygen, water, microorganisms and metal sulfide materials and therefore reduces AMD formation. However, such methods do not always successfully prevent the formation of AMD and are difficult to implement in practice. While source control approaches are a focus for future research [5], a more realistic and common approach is to treat the generated AMD and leachates. Generation of AMD and leachate from tailings storage facilities at both active and historic mine sites is predicted to continue over a multi decadal time span and will therefore need corresponding long-term treatment. However, long-term treatment presents a difficulty, particularly where active treatment processes **Table 1** [6] require indefinite operational and maintenance inputs, which incur large costs, including long-term energy usage and treatment of metal rich sludges [7].

Given the costly, unsustainable and largely unknown operational timescale for active treatment processes for acid mine leachates, there has been a focus in the past 20+ years on passive treatment technologies, which tend to have lower capital

Active treatment process	Summary description
Chemical precipitation	Precipitates are formed by addition of chemicals such as metal hydroxides and are separated from the water by sedimentation and/or filtration
Ion exchange	Synthetic or natural resins are used to exchange cations with soluble metals in the wastewater
Membrane filtration	Technology which uses different types of membrane filtration methods such as ultrafiltration, reverse osmosis, nanofiltration and electrodialysis to separate solutes from the water across semi-permeable membranes
Coagulation and flocculation	Colloidal particles are destabilized by charge neutralization so that they agglomerate into larger flocs which settle more readily as a metal rich sludge

Table 1.
Summary descriptions of some active treatment processes for removal of heavy metals from acid mine leachates.

construction costs and generally rely on gravity rather than pumped flow. They also require much lower operational and supervision inputs, although some level of maintenance will be required to ensure effective removal efficiency. Passive treatment technologies also do not require continuous chemical inputs and are therefore more sustainable than active treatment processes; however their ability to effectively treat mine waste streams in the long-term is largely unknown [7]. The key characteristics of passive treatment systems are their ability to produce alkalinity and to efficiently remove metals from the leachates. Some of the more promising passive treatment technologies are assessed below.

2.1 Neutralization

Given that pH is an important influence on trace metal solubility, passive treatment by neutralization is sometimes used to remove metals from acid mine leachates. One such method is the installation of oxic or anoxic limestone drains where acidic mine leachate is directed through the bedding material and neutralized to a pH ≈ 6 by dissolution of the limestone. The alkalinity production and neutralization rates are important criteria when selecting the limestone, as a high carbonate content induces quicker neutralization rates. An operational drawback with limestone drains however is that long-term metal hydroxide precipitation tends to clog the limestone and reduce their flow capacity. This can be overcome somewhat by use of anoxic drains, which inhibit the formation of these precipitates; however, accumulation of other particulate material within the drains also contributes to reduced permeability of the drains over time [8]. In addition, removal of some metals, such as Zn and manganese (Mn), require a pH < 6, which is lower than the pH that can be naturally provided by passive limestone drains. In such cases, alternative or additional treatments such as Dispersed Alkaline Substrate (DAS) systems may be used. These may include application of fine-grained alkaline reagents to provide high neutralizing capacity, such as magnesium oxide (MgO) powder or limestone sand mixed with high porosity inert materials to ensure continuous flow through the medium [9, 10].

Other alkaline waste byproducts, such as fly ash (FA) and bottom ash (BA), flue gas desulphurization material, recycled concrete aggregate (RCA) and alkaline industrial byproducts have also been investigated as potential alternatives to traditional treatment materials. A leach test study to evaluate and compare the efficacy of RCA and FA in remediating AMD found that while RCA's were effective in neutralizing AMD and reduced concentrations of iron (Fe), Cr, copper (Cu) and Zn, FA's actually increased Fe, Cu and Mn concentrations. In addition, RCA with a higher calcium oxide content and finer grained particles had greater efficacy in increasing the pH and reducing concentrations of magnesium (Mg), Mn and Zn in the AMD [11]. In a separate laboratory based filtration study to investigate the effectiveness of alkaline industrial byproducts, namely drinking water treatment residuals (WTR's), to neutralize and remove metals from AMD, the authors reported irreversible removal of more than 99% of Fe, Al, Zn, lead (Pb), As, Mn and 44% of sulfate (SO_4^{2-}) [12].

Natural neutralization of AMD has also been reported in two abandoned alum shale pit lakes, which originally contained acidic waters (pH < 4) with elevated levels of Na, K, Mg, calcium (Ca), Al, Mn, Fe, and sulfate. Inflow of leachates from an adjacent alkaline waste deposit gradually increased the pH from <4 to 8, which resulted in decreased concentrations of Fe, Al, Co, Ni and Zn in the lakes. However, accumulation of metal laden sediments in the lakes pose a long-term threat in the

event that the lakes become re-acidified over time, leading to desorption/dissolution of trace elements. Thus, the long-term effects of changing lake chemistry in natural neutralization processes may alter the distribution and concentrations of trace elements with time in the lake outflows and this needs to be considered in the context of a sustainable solution [13].

2.2 Adsorption/biosorption

Although considered by many as an active treatment process, adsorption, and in particular biosorption, is considered to be an efficient treatment method which uses abundantly available waste organic material and biomass to adsorb toxic contaminants, such as heavy metals, from wastewaters. Depending on the biomass used, biosorption of heavy metals occurs via electrostatic interactions or hydrogen bonding due to the formation of carboxyl groups on the adsorbents for binding cationic metals and amine groups for binding of either cationic or anionic metals [14]. Biosorption also offers the possibility of adsorbent regeneration and metal recovery while producing a minimal amount of chemical sludge. While many biosorption studies have examined the uptake of single metals with a variety of results (**Table 2**), adsorption of multiple metals is more difficult where competing ions reduce the capacity of the adsorbent to remove target metals [23]. For example, in a batch study to investigate the effectiveness of waste digested activated sludge (WDAS) as a biosorbent to remove and recover metals from AMD, the authors reported high (>70%) removal of V and Cu, and slightly lower (40–70%) removal of uranium (U), thorium (Th) and Cr; however the removal

Metal	Biosorbent	Solution pH	Maximum Uptake (mg g–1)	Reference
Pb(II)	Sewage sludge	5	98.5	[15]
Cd(II)		5	67.3	
Cu(II)		5	48.7	
Cr(III)	Garden grass	4	19.4	[16]
Cr(III)	Fugal biomass of *Termitomyces clypeatus*	4	24.8	[17]
Ni(II)	Activated carbon (peanut shells)	4.8	26.4	[18]
Mn(II)	Activated carbon (bone char)	5.7	22	[19]
Cu(II)	Rice straw	6	12.3	[20]
	Rice husk	6	8.9	
Cd(II)	Rice straw	6	9.1	
	Rice husk	6	1.6	
Cu(II)	Algal biomass (*Cystoseira crinitophylla*)	4.5	160	[21]
Fe (as $FeSO_4.7H_2O$)	Shrimp shells	2.8	17.4	[22]
Mn (as $MnSO_4.H_2O$)		2.8	3.9	

Table 2.
Metal uptakes from acid mine drainage by a variety of natural biosorbents.

rates were dependent on WDAS concentrations. The authors also noted that that there was no removal of Mn, Ni, Zn and yttrium (Y) at any WDAS concentration [24].

While many laboratory scale biosorption studies have been carried out for the removal of heavy metals from AMD, the development of full-scale biosorption treatment systems is at an early stage. Like many filtration systems, operational issues such as clogging of the adsorbent pore spaces and the need to recycle spent adsorbents are difficult issues to overcome and ultimately lead to increased maintenance. However, the possibility of resource recovery from such systems may eventually be a consideration for their full-scale development.

2.3 Constructed wetlands

Constructed wetlands (CW's) are a passive wastewater treatment technology that combine biogeochemical and physical interactions between the wetland's soil matrix, vegetation and microbial communities. Constructed wetlands may be categorized in terms of their hydrology (whether surface or subsurface flow), their flow path (whether horizontal or vertical) and the type of macrophytic growth (whether free floating, submerged or emergent plant growth) [25]. When treating AMD, some or all of these components can be adjusted to suit the local and environmental conditions making CW's very flexible and efficient treatment systems. The key components and operating parameters for effective and efficient operation of a CW include: number of cells within the CW, substrate type and composition, plant type and planting density, hydraulic flow paths, hydraulic loading rate and hydraulic retention time. Wastewater pH is a key treatment indicator for AMD as it affects metal removal efficiencies. In a bench scale study to evaluate the performance of a CW using a mixed substrate of 75% soil, 20% powdered goat manure and 5% wood shavings, the pH of the AMD increased from 2.93 to 7.22 within 24 hours with corresponding enhanced removal rates for Fe (95%), Cu (90%), Zn (77%), Pb (89%), Co (70%), Ni (47%) and Mn (56%). In addition the sulfate content of the AMD decreased by an average 25% with an increase in alkalinity from 0 to 204 mg $CaCO_3$ L^{-1} [26]. The authors attributed the sulfate reduction to the addition of biodegradable organic substrate to the soil (in the form of goat manure and wood shavings) which provided a carbon source for the anaerobic microbes to generate alkalinity, leading to sulfate reduction and associated metal removal.

Leachate metal removal by CW's include physical, chemical and biological processes which are both complex and interactive. The metal removing mechanisms include sedimentation, sorption, precipitation, cation exchange, photodegradation, phytoaccumulation, biodegradation, microbial activity and plant uptake [27]. During CW treatment of acidic and alkaline leachates, many metals are precipitated from solution, because of a change towards circumneutral pH (**Figure 1**). Once this happens, they settle through the liquid and into the substrate /sediment of the CW, provided flow conditions are sufficiently acquiescent. For example, Fe, Al and Mn can form hydroxides through hydrolysis and/or oxidation, which deposit in the substrate. The rate of change in pH varies as the effluent moves through the CW and this determines how quickly precipitation will occur and also the locations where most sedimentation occurs. If pH changes quickly it can be expected that metal accumulation in the sediment will occur at the inlet end of the CW and conversely if pH changes are slow then metal accumulation will be more dispersed. The retention time of CW's are therefore important design considerations. While settled
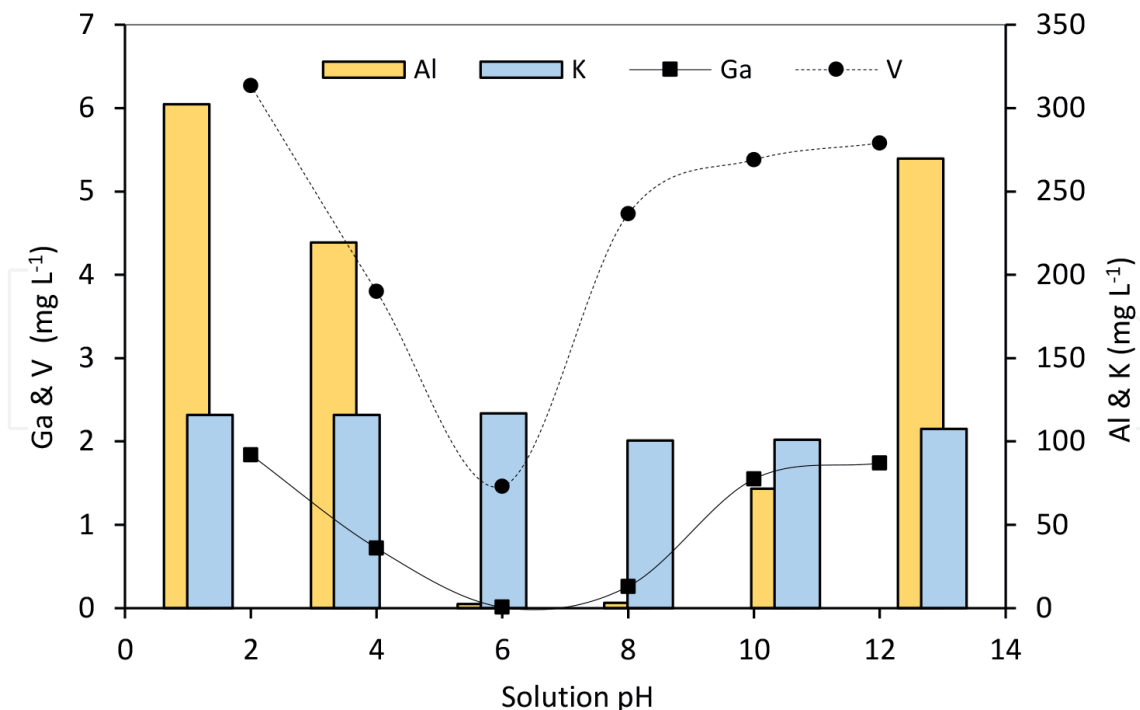
Figure 1.
Metal solubility versus solution pH for a selection of synthetic amphoteric metal solutions [unpublished data].

metals will ideally remain in the sediment indefinitely, there is a risk that long term changes in the pH may result in resolubilisation and emission of high metals concentrations in the treated effluent. Such a risk is related to the composition of the substrate/sediment and the amount of organic matter it contains [26]. As well as precipitation and sedimentation, adsorption of the metals by the soil is probably one of the more significant metal removal processes in CW treatment. Metal adsorption occurs either by reversible cation exchange or by irreversible chemisorption. Adsorption to humic or clay colloids is more permanent than adsorption to soil organic matter which ultimately decomposes and releases the adsorbed metals back into solution. The role of biological processes for metal removal in CW's is an important one, and these are normally centered around the wetland plants. As well as providing direct uptake of metals from the wastewater, wetland plants generate organic particulate matter that contributes to sedimentation processes and to symbiotic bacterial processes. Plant species, particularly emergent macrophytes such as *Phragmites* or *Typha* species, also influence the rhizosphere. Root exudates and oxygen gradients within the sediment/substrate can facilitate diverse microbial communities that can influence the oxidation state in the sediment and partial pressures of CO_2 or O_2 in solution, influencing metal removal [28]. The rate of metal uptake by plants varies significantly, depending on plant type (emergent, surface floating, or submerged), species, density, and growth rates with maximum uptake observed in the roots [29].

The long-term performance of CW's to treat AMD is variable with effectiveness determined by variables such as metal types and concentrations in the influent and the quality and quantity of the wastewater. Typically, removal of the contaminants Fe, Al and Zn is highly effective in both the short (1–3 years) and longer term (c.10 years). However, other metals, such as Mn, are more problematic and lower removal rates have been reported [7].

3. Treatment of alkaline leachates

Many of the processes used to treat AMD described in the previous sections are similarly used to treat alkaline leachates generated at disposal sites of industrial by-products. Neutralization or partial neutralization of alkaline leachates prior to discharge to a pH of approximately 8.5–9 using acids is a commonly used treatment process. Recent attempts have been made to examine passive neutralization techniques such as passive in-gassing of atmospheric of CO_2 [30], seawater and industrial waste brines [31]. Apart from proximity to an available supply, one of the main disadvantages of seawater neutralization is the high amount of seawater needed and so use of concentrated brines have also been investigated, mostly limited to laboratory studies [31]. Use of CO_2 may ultimately provide an attractive neutralization option for alkaline leachates, particularly if CO_2 emissions from the processing plant or from adjacent industries could be recycled, thereby reducing their carbon footprints. However, while passive remediation using CO_2 has been examined at a laboratory scale [30], further investigation is required at a pilot scale to evaluate issues such as pH rebound. To overcome this, a hybrid process combining CO_2 and brine treatments might be considered where the CO_2 converts hydroxides to insoluble carbonates and bicarbonates leading to a more stable leachate with a pH < 8.5 [31].

Biosorption of alkaline leachates has also been investigated with varying degrees of success. There are many factors which influence the metal adsorption capacity of biosorbents, including biosorbent characteristics such as pore volume and specific surface area, ionic strength, contact time, adsorbent dosage, solution temperature, initial metal concentration, and solution pH. Solution pH is one of the more important factors, particularly where electrostatic interactions play a key role in the adsorption process such as metal removal from alkaline leachates. The pH at which the net surface charge of the adsorbent is zero is termed the zero point charge (pH_{zpc}). When the pH is less than the pH_{zpc}, the adsorbent surface becomes positively charged and therefore has a high affinity towards negatively charged or anionic metal species. Conversely, when the pH is greater than pH_{zpc}, the surface becomes negatively charged and has an affinity towards positively charged or cationic metal species. In general, optimum metal adsorption is more common at acidic rather than basic pH values, given that alkali metals form cations, which are not attracted to protonated functional groups on the adsorbent surfaces. For example, in a batch study to investigate the efficacy of red mud modified sawdust biochar to adsorb V from aqueous solution, the authors reported a maximum uptake of 16.5 mg g^{-1} at a solution pH in the range of 3.5–5.5. They attributed the higher uptake levels at low pH to the positively charged adsorbent surface, which enhanced its binding capacity for anionic metal species in solution [32]. However if the pH_{zpc} of the adsorbent is relatively high, then this may promote the removal of heavy metals in alkaline solution. In a batch study to measure the uptake of Cu(II) and Cd(II) from aqueous solutions using ferromanganese binary oxide-biochar composites with a pH_{zpc} = 9.2, the authors reported maximum uptakes of 64.9 and 101 mg g^{-1} respectively, which increased as the pH increased from 3 to 6. Other adsorption studies at high pH values have also been reported (**Table 3**).

The use of CW's to treat alkaline leachates has also proved successful and as for AMD, the treatment processes rely on metal precipitation, sedimentation, sorption, biological activity and vegetation. The ability of CW's to buffer pH is a key treatment mechanism and recent studies have shown that CW's are effective in quickly reducing

Metal	Biosorbent	Solution pH	Maximum Uptake (mg g−1)	Reference
Cr (VI)	Ground nut shell	8	3.8	[33]
Ti (I)	Manganese dioxide coated magnetic pyrite cinder	12	320	[34]
Cd (II)	Cashew nut shell resin bonded with magnetic Fe₃O₄ nanoparticles	10	54.6	[35]

Table 3.
Selection of metal adsorption studies at high pH values.

pH from pH ≈ 11–13 to pH ≈ 7–10 with associated reductions in concentrations of Ca, Al, Ba, Cr, Ga, Ni, Zn and V; however a pH < 10 was needed for effective V reduction [35, 36]. Similar to AMD treatment, the use of CW's to treat alkaline leachates is an attractive long term passive treatment option; however while their longevity in the short term (ca 5 years) has shown to be effective, there is a lack of data to assess their long term performance, particularly with regard to metal concentrations and metal forms in the sediments [7]. While there is no evidence to date of metal accumulation in the CW vegetation treating alkaline leachates [35, 36], the long-term risks of metal saturation in the sediment and metal resolubilisation due to pH changes with concomitant increase in treated effluent concentrations needs to be assessed over a sustained period and under varying operating conditions to establish the long term viability of CW's.

4. Resource recovery from acidic and alkaline solid wastes and leachates

Large quantities of acidic and alkaline wastes are disposed of in storage facilities generating large quantities of metal rich leachates, which are potentially valuable but also toxic to the environment. Several attempts have been made to recycle these wastes but currently waste production far outstrips demand for their reuse. Potential uses for these waste materials are discussed below, many of which focus on the construction industry as an outlet.

4.1 Recycling of mine wastes

Mine tailings have been trialed for use as additives for the production of cement, building bricks and road construction materials, mainly aggregates and asphalt. The use of electric arc furnace steel slag and copper mine tailings were investigated as suitable substitutes for granite aggregates in road asphalt mixtures and were found to improve their performance when compared with conventional aggregates [37]. Similarly, magnetite tailings were used as a substitute for limestone aggregate in asphalt mixtures and were found to improve their high temperature properties and slightly decrease their splitting strength at low temperature [38]. The impact of copper mine tailings blended with cement mortars was also investigated and results indicated that their addition enhanced the mechanical strength of the mortar as well as increasing their resistance to chloride and acid attack [39]. Other studies however have noted that use of mine tailings for cement production involves increased energy consumption, increased dust generation and large emissions of CO_2, and have instead advocated the use of geopolymerization as a sustainable process. Geopolymerization chemically

binds natural occurring silico-aluminates to form a stable material (geopolymer) with an amorphous polymeric structure. It has an advantage over other recycling processes in that it reduces the leaching potential of the waste, locking about 90% of the metal content into the geopolymeric matrix [39]. This process therefore requires mine tailings, which are rich in silicon (Si) and Al, both of which are essential materials for geopolymerization. Although an emerging technology, potential applications and properties of geopolymers are their high mechanical strength, good durability, good fire resistance (up to 1000–1200°C without loss of function) and are fast setting making them suitable for use as construction materials such as geopolymer concrete. They also have low energy consumption and generate low waste gas during manufacture with associated reduced CO_2 emissions (≈80% reduction) when compared with production of Ordinary Portland Cement [39]. However, as with many innovative emerging technologies, the long-term release of toxic metals from geopolymers requires further research in relation to its eventual leachability during weathering.

Sludge produced from AMD has also been used as an adsorbent for treatment of agricultural waste. In one such column study, the authors reported that AMD sludge was potentially an effective low cost adsorbent for the removal of phosphate from dairy wastewater [40]. It is worth remembering however, that pollution swapping must be considered when applying new recycling technologies and care should be taken not to increase one pollutant as a result of introducing a measure to reduce a different pollutant. For example while one pollutant (phosphorus) might be reduced, metals associated with the adsorbent may be released in the long term and this need to be assessed as part of a life cycle assessment (LCA) to evaluate the overall environmental impacts.

Metal recovery from AMD (as opposed to acid mine waste) remains a technically difficult process where selective precipitation remains the most common treatment method. Separation of a particular metal from a matrix of other metals in solution is a difficult one and typically involves an integrated process, particularly at low metal concentrations. The viability of such processes depends on the economic value of the target metal to be recovered as well as its relative concentration. Treatment technologies such as microbial fuel cells, biological sulfide precipitation, sulfate reducing bacteria, membrane separation and adsorption remain the most promising recovery methods in conjunction with coagulation and precipitation processes and the use of aeration and oxidation to improve efficiencies. While these technologies present opportunities for metal recovery, there are also challenges with their development, not least their economic and environmental viability. It is worth noting that, in addition to trace metals, water, rare earth metals and sulfuric acid are also valuable resources contained within AMD discharges.

4.2 Recycling of alkaline wastes

4.2.1 Municipal solid waste incineration byproducts

The final residue after MSW incineration is generally <10% of the original volume and < 30% of the original mass and typically comprises (i) bottom ash, made up of non-combustible organic matter and inert materials such as glass, ceramics and metals; (ii) grate siftings, fine materials which pass through the grate and are collected at the base of the combustion chamber; (iii) boiler and economizer ash, coarse particulate matter contained in flue gases and usually collected at the heat recovery section; (iv) fly ash, fine particulate matter downstream of the heat recovery section and (v) air pollution control (APC) residues in the form of particulate

material captured prior to gas emissions to the atmosphere. The amounts of residue generated depend on the composition of the MSW, and the type and efficiency of the incineration process; however typical quantities, expressed as a percentage of the original waste mass on a wet basis, are 20–30% for bottom ash and grate siftings, 10% for boiler and economizer ash, 1–3% for fly ash, and 2–5% for APC residues.

Treatment and disposal of incineration ash residue varies considerably between countries. In China for example most of the bottom ash, an estimated 11 Mt. annum^{-1}, is disposed directly to landfill without pretreatment while in France, Denmark and the Netherlands 80, >90 and 100% respectively of bottom ash is used for road construction and embankments with the balance sent to landfill [41]. Similarly, in countries such as Belgium, Germany, Norway, Spain and Sweden reuse of bottom ash is incentivized resulting in ongoing efforts to establish new outlets for its reuse [42]; however, in the USA almost all incinerator ash is sent to landfill [43].

Typically, scrap iron and other metals are recovered from bottom ash before being landfilled or reused in the manufacture of different types of construction materials. Such applications may be commercially viable but have limitations, for example if ashes with high salt concentrations are used in the manufacture of cement, this may lead to accelerated corrosion of steel reinforcement. Bottom ash is most frequently used as a road granular sub-base material but is more susceptible to leaching in unbound aggregate than in cement bound or ceramic materials which lock in the heavy metals thereby restricting their leachability [44].

Recycling of fly ash, boiler and economizer ash, and APC residues on the other hand is at very low levels with almost all of these being landfilled [41], although other treatments such as thermal processing (melting technology) are also used [45]. The main reason for high disposal rates of fly ash to landfill is that fly ash typically contains high concentrations of heavy metals (for example Zn concentrations can be as high as 60,000 mg kg^{-1}), salts and organic micro pollutants due to their volatization and subsequent condensation during the incineration process. For this reason, fly ashes have a low reuse potential, for example in the cement industry, compared to other secondary raw materials. They are therefore classified as hazardous waste in many countries, which is disposed to either hazardous waste landfills or cement stabilized prior to disposal to non-hazardous waste landfill sites. Similar to bottom ash, one of the main environmental difficulties with recycling fly ash is its leaching potential and consequently there is an emphasis on improving its quality so that it can be used in more sustainable applications.

4.2.2 Industrial waste incineration byproducts

Coal fired power plants are one of the main global energy sources and currently contribute over 40% of power generation. Consequently coal combustion ashes are a major source of economic and environmental concern with >750 Mt. coal ash generated annually and < 50% reused with the remainder generally disposed to landfill or impounded. In Germany for example, approximately 10 million tonnes of stabilized ash is produced annually from lignite combustion power stations [46]. Globally, approximately 25% of coal fly ash is reused with the remainder disposed as waste to landfill. Coal fly ash is an alkaline residue with a variety of trace metals including barium (Ba), boron (B), cadmium (Cd), Co, Cu, Cr, mercury (Hg), Ni, Pb, Mn, tin (Sn), strontium (Sr) V and Zn [47]. While some of these metals are attenuated, at least in the short term, by the alkalinity of the fly ash, other oxyanionic species are released with consequent adverse environmental impacts. Recent research has focused on their

recovery as critical and rare earth elements. Similar efforts are being made with regard to other industries including the steel industry and hazardous waste incinerators. In Sweden for example, trials have indicated recovery of >95% Fe and Mn, and 40% Zn from bottom ash from a crushed alkaline battery incinerator. These represented the metals with the highest concentrations in the bottom ash (Fe, 143,800 mg kg^{-1}; Mn, 154,600 mg kg^{-1} and Zn, 65,810 mg kg^{-1}). In a separate hazardous waste incinerator trial, valuable metals such as Ni, Sb, Mo, Zn, Cr, and Cu were recovered along with significant quantities of soluble salts, which can be subsequently used as deicing agents on motorways [unpublished data].

4.2.3 Bauxite residue reuse

Bauxite residue is characterized by extreme alkalinity (pH $\approx$ 10.5–13.5), its red color due to high Fe_3O_3 content ($\approx$10–50%) and its similarity to clay in terms of its mechanical and physical properties. It also has high concentrations of aluminum oxide (Al_2O_3, < $\approx$10–20%). The extreme alkalinity and leachability potential are the main barriers to its reusability, which is considered to be mainly in geotechnical engineering applications [48]. However, given its low strength, poor hydraulic conductivity and relatively poor compactability, additives may be required to render it suitable for many applications including as a road construction material [48]. Changes (reductions) in pH over time may also contribute to long-term leaching, resulting in potentially toxic metals being released to the environment and further research is needed to assess for example the application of pozzolanic materials as a low cost stabilization method.

The application of bauxite residue as an additive to masonry materials has also been investigated. For example, in a study to evaluate the use of bauxite residue co-mixed with agricultural residues as an additive to replace clay in the production of ceramic bricks, the authors concluded that samples produced with an additive of 10% hazelnut shells and 30% bauxite residue resulted in acceptable thermal conductivity and compressive strength values (0.45 W/mK and 9 MPa respectively). Importantly the authors reported that leaching toxicity values were within acceptable Environmental Protection Agency limits [49].

Similar to AMD, metal recovery from alkaline leachates is a technically difficult process, which tends to rely on selective metal precipitation. In a study to investigate V adsorption from aqueous solution by potassium hydroxide (KOH) modified seaweed hydrochar, the authors assessed the reusability of the adsorbent and found that while the adsorption levels remained consistent over three cycles, the physical condition of the adsorbent was the limiting factor in terms of recycling [50]. Thus, further investigation of low cost organic biosorbents in terms of mechanical and physical parameters such as particle size, hydraulic conductivity and porosity in a continuous flow system, as well as life cycle assessment are needed to develop the technology to a higher level.

5. Conclusions

Production of acidic and alkaline mine wastes is expected to continue into the future, with ever increasing amounts of acid mine drainage and alkali leachates being

generated over a multi decade timescale. The detrimental impacts of these leachates on the aquatic environment is evident with in excess of 18,000 km of streams polluted or projected to be polluted from the coal mining industry alone in north America. Global treatment and remediation costs for existing and abandoned mines is significant, estimated in the range \$32–72 billion, while the remediation costs of treating AMD at abandoned mine sites is estimated to be higher than at operational sites. The difficulty with treatment of acidic or alkaline leachates is that metals tend to exist in low concentrations and in complex matrices. Current active treatment processes such as chemical precipitation, ion exchange, membrane filtration, and coagulation and flocculation processes require ongoing chemical and maintenance inputs, energy usage and treatment of metal rich sludges. To overcome these disadvantages, there has been a recent emphasis on developing passive and sustainable treatment solutions, which do not require continuous chemical and energy inputs. Passive treatment methods such as neutralization, adsorption/biosorption and constructed wetlands are considered to be some of the more promising techniques; however they are not yet fully proven and their ability to effectively treat AMD and alkaline leachates in the long-term is largely unknown. These and other technologies, including hybrid solutions, require further research for long term and sustainable treatment.

Many attempts have been made to reuse disposed acidic and alkaline wastes; however their production far outstrips their demand for reuse at present. The construction industry is a key outlet for mine and industrial waste reuse in products such as aggregates for road construction, cement manufacture and masonry materials. For many applications however, the long term performance of recycled wastes is uncertain and in many cases their use may require increased energy inputs resulting in higher CO_2 emissions when compared with traditional materials. To overcome these disadvantages, recent developments of geopolymer based products, formed from Si and Al rich mine tailings, are regarded as a promising emerging technology. Geopolymer based products have good mechanical and durability properties, which potentially make them suitable for use in a wide variety of construction materials. Additionally, the geopolymerization process binds in metals thus reducing their potential for long-term leaching.

With the identification of some metals as 'critical' for modern technology and their availability unpredictable, there has been a recent interest in examining routes to recover such valuable and sometimes scarce metals from mine and mineral processed waste. Metal recovery from the large volumes of leachates generated from acidic and alkaline wastes have had limited success, predominantly due to the complex nature of the metals which tend to exist in low concentrations. However, recent studies have reported efforts to enhance the metal adsorption properties of abundantly available biowaste materials which are sourced from other industries (e.g. agriculture/ aquaculture industries) to facilitate selected metal recovery from mine and industrial leachates. This type of research fits well with the circular economy model of production and consumption, and reinforces the idea of using biowaste from one industry as a raw material to recover valuable resources from another. Although promising, these and other research developments need further technological and life cycle assessments to enhance their technology readiness levels, prior to implementation at an industrial scale.

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Conflict of interest

The authors declare no conflict of interest.

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