

Minerals and Mine Drainage

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ABSTRACT: A review of the literature published in 2012 on topics relating to acid mine drainage (AMD) or acid rock drainage (ARD) due to the presence of sulfide bearing minerals in active and abandoned coal/hard rock mining sites or waste spoil piles is presented. This review is divided into the following sections: 1) Characterization and Assessment, 2) Protection, Prevention and Restoration, 3) Toxicity Assessment, 4) Fate and Transport, 5) Biological Characterization, and 6) Treatment Technologies. Due to the complexity of the minerals and mine drainage, many papers presented in this review address more than one important topic, indicating that they can be categorized into more than one section. Therefore, the different sections presented in this review should not be regarded as being mutually-exclusive or all-inclusive.

KEYWORDS: mine drainage, acid mine drainage, acid rock drainage, mine water, mine waste, sulfate, sulfate reducing bacteria, AMD treatment

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Characterization and Assessment

Site Characterization. An important aspect of acid mine drainage (AMD) or acid rock drainage (ARD) study is to characterize the contaminants released into the environment. The trace element concentrations in soils, sediments, and natural waters were studied in the "Geita Gold Mine" (GGM) and "North Mara Gold Mines" (NMGM), in Northwest Tanzania (Almas and Manoko, 2012). A great variation was observed in type of elements and intensity of their spill to soils, sediments, and waters.

The geochemistry and mineralogy of samples collected along depth profiles from an As-rich tailing deposit with abundant calcite was studied to determine the processes that influenced the mobility of Fe, Zn, Cu, Ni, Cd, As, Sb, Cr and Tl in Zimapán, Central Mexico (Armienta et al., 2012). Total concentrations decreased as: Fe>As>Zn>Pb>Cu>Sb>Cd>Cr>Ni>Tl. Mobility decreased as: Tl>Cd, Zn, Cu, Sb, Ni, As>Fe, Pb>Cr. Higher soluble concentrations of Fe, Cu, Zn, As, Pb, and Ni were present in low-pH samples and of Sb and Tl in near-neutral samples.

The spatial distribution of the chemical elements released during the sulfide- and gangue-mineral alteration was evaluated (Carbone et al., 2012). In particular,

the mobility of Ni, Cu, Zn, As, Se, and Mo appeared to be controlled by the goethite genesis through several mechanisms such as structural incorporation (Ni), coprecipitation, and/or adsorption.

An initial evaluation of the effects of Mn mining on water quality in the Chiatura region, Republic of Georgia was performed ([Caruso et al., 2012](#)). Although Mn and Fe oxide solids found in sediment could increase adsorption and attenuation of other metals from water, the contaminated sediments could also serve as a long-term source of metal contamination with potentially significant adverse ecological and human health effects.

At the Ore Knob tailings pile (Ashe County, North Carolina, USA), significant spatial variations in the physical and hydraulic characteristics of the tailings caused large variations in air-filled porosity and effective oxygen diffusion into the pile ([Behrooz and Borden 2012](#)).

The characterization of the Rio Mannu basin according to Italian protocols was carried out to evaluate the levels of contamination in each mine area and the risks in the plains surrounding the site ([Cidu et al., 2012a](#)). The characterization plan could be a relatively cheap tool to establish mitigation actions prior to a complete (usually expensive) remediation project at abandoned mine sites.

Characterization of the present conditions of the San Cristobal and Las Moreras riverbeds in the Mazarron district, Murcia (SE Spain), revealed significant toxic metal and metalloid contents (Ag, As, Cu, Sb, Pb, and Zn) in the alluvial materials from both riverbeds ([Martin-Crespo et al., 2012](#)). An important level of contamination by

AMD from the surficial tailings to the watercourse sediments and waters was also observed.

Characteristics of groundwater 10 years after the spill caused by the rupture of the Aznalcollar tailings dam into Agrio and Guadamar rivers were studied ([Olias et al., 2012](#)). The concentration of toxic elements was mainly controlled by pH. A sharp decrease in contaminant levels after the first years was observed which was followed by a subsequent stabilization.

Oyarzun *et al.* ([2012](#)) analyzed the contribution of (a) acid drainage from the Andean epithermal El Indio Au-Ag-Cu-As district and nearby hydrothermal alteration zones, and (b) diffuse sediment dispersion from abandoned tailings deposits to the current metal contents of the fine grained sediments of the rivers and creeks of the Elqui basin. It was found that As pollution (0.03%) was mainly derived from the El Indio district and potentially toxic heavy metals (notably Cd, Pb, Hg and Mo) were present in low concentrations.

The examination of lake sediment cores near two sulfide mines (Ylojarvi and Haveri) in SW Finland was conducted to assess the long-term evolution of metal and metalloid drainage from mining areas including pre-mining conditions ([Parviainen et al., 2012](#)).

In an abandon gold and silver mine in Furtei, Sardinia (Italy), sulfide-rich materials were left on site resulting in highly contaminated drainage flowing downstream from the mine, which posed a hazard to the agricultural areas ([Cidu et al., 2012b](#)).

EXAFS spectroscopy was employed to investigate the formation and identify the structure of aqueous uranyl arsenate species at pH 2 (Gezahegne et al., 2012). The two species that would be present in acidic uranium-arsenic-rich solutions were thus $\text{UO}_2\text{H}_2\text{AsO}_4^+$, and $\text{UO}_2(\text{H}_2\text{AsO}_4)_2^0$.

Ettringite-gypsum sludge, formed by neutralization of AMD with lime, was examined with standard leaching and sequential extraction procedures (Gomes et al., 2012). It was found that the sludge could be sources of dissolved F, SO_4 , Fe, Zn, Mn, U, and Al under various environmental conditions, although it was classified as non-toxic by standard leaching protocols.

The geochemical characteristics of surface water and stream sediments was examined to establish the geochemical baseline conditions prior to any type of new mining activities in the Asprolakkas drainage basin, an area of tertiary mineralization within amphibolite, located at NE Chalkidiki peninsula, Greece (Kelepertzis et al., 2012).

The presence of heavy metals in water and sediments of the Yacoraite River Jujuy Province, NW Argentina, was characterized for source identification (Kirschbaum et al., 2012). The seasonal variation of heavy metals concentration in water and the impact on water quality were observed.

To evaluate internal physical structure and geochemical characteristics of coal mine overburden dumps, a series of field investigations, physical and

geochemical laboratory characterization were conducted (Kusuma et al., 2012). It was found that the internal structure formed and the spatial heterogeneity of geochemical characteristics in overburden dump controlled the acid drainage inhibition process within the dumps.

The pH was a major control on the spatial variation pattern of soluble, exchangeable, and carbonate-bound Cu, Zn, and Cd in a stream system affected by AMD (Lu et al., 2012c). Metal distribution was also controlled by the abundance of organic C, carbonate C, and oxides of manganese and iron (Lu et al., 2012c).

Characterization of the ochre precipitates and the mine water effluents of some old mine adits and settling pits after mining of polymetallic ores was performed in Slovakia and it was found that the dominant phases were ferrihydrite with goethite or goethite with lepidocrocite (Maa et al., 2012).

Geochemical characteristics of dissolved metals including the rare earth elements (REEs) in AMD from the Jaintia Hills coalfield, Meghalaya were studied (Sahoo et al., 2012a). The mine drainage was characterized by low pH with high concentrations of Fe, Al, Mn, Ni, Pb and SO_4^{2-} and REEs. The average total REE concentration in AMD was 714.7g/L and REE pattern indicated that streams were highly impacted by the AMD.

REE concentrations in the bedrock samples from the Sitai coal mine and the Malan coal mine in Shanxi province, China, were identified to be one order of magnitude higher than those found in pyrite and coal

samples ([Sun et al., 2012](#)). The high REE concentrations in AMD were most likely caused by the acidic solution leaching REE out from the bedrocks. The data was further analyzed through adsorption and desorption experiment and hydrogeochemistry software PHREEQC.

The iron-rich precipitates from AMD sites around the Jaintia Hills coalfield, India, were mainly schwertmannite, goethite, and jarosite ([Sahoo et al., 2012b](#)). Ni, Mn, Cr, Cd, Pb, and Zn were more significant in schwertmannite-bearing ochre than in more crystalline jarosite- and goethite-bearing ochres. Metal mobility was mainly controlled by the Fe and Mn oxyhydroxide phases.

Significant discrepancies in the hazardousness classification of the dispersed alkaline substrate (DAS) residues was observed according to the US EPA TCLP or European standard leaching test EN 12457-2 ([Macias et al., 2012a](#)). The absence of some important metals (like Fe or Al) in the regulatory limits employed in both leaching tests severely restricted their applicability for metal-rich wastes testing.

Assessment and Monitoring. A comprehensive geochemical assessment of the potential environmental impact was conducted in the Klip River coalfield, Kwazulu-Natal Province of South Africa ([Zhao, 2012](#)). Because the majority of the samples had sulfide-sulfur higher than 0.25%, the two dumps had the potential to turn acidic based on the acid base accounting results. There was

also a concern with heavy metal leaching, specifically Al, Fe, Mn, and Zn from the dumps.

Analyses of solid phases and water, speciation modeling, and multivariate statistics were conducted to examine the contamination of the Kafue River network in the Copperbelt, northern Zambia ([Sracek et al., 2012](#)). The observed high metal content in stream sediments might be a potential environmental risk if the metals in sediments were to be re-mobilized during accidental acid spikes.

The environmental risks due to acid rock/mine drainage and the metal leaching potential of multiple mines of gold and manganese on the Ankobra River Drainage Basin in Southwestern Ghana was assessed ([Akabzaa and Yidana, 2012](#)). Sulphide-bearing lithological units with profound compositional variations were due to the incorporation of potentially toxic heavy metals and metalloids associated with carbonates and silicates. Zn, Cu, Ni, As, Co, Sb, SO_4^{2-} , pH, alkalinity and conductivity were adequate parameters in routine environmental risk monitoring programs of mines in the area.

A review of the impacts of deep metal mine water discharges on riverine sedimentology, hydrology, and ecology and strategies for the restoration of rivers draining historically abandoned metal mines was performed by Byrne *et al.* ([2012](#)).

Hernandez *et al.* ([2012](#)) developed a physically-based numerical model that incorporated new approaches for a finite element solution to the steady/transient

problems of the joint surface/groundwater flows of a particular region with the help of a Geographic Information Systems to store, represent, manage and make decisions on all the simulated conditions. Barnes and Vermeulen (2012) provide a comprehensive guide to the establishment of a groundwater monitoring programme in South Africa for environmental practitioners in the coal industry.

An exploratory investigation was performed to evaluate the potential impacts of mining activities on soil and water environments at the Shivee-Ovoo coal mine area in Mongolia and the open-pit mining of the study area showed no obvious environmental impact at present in its vicinity (Battogtokh et al., 2012).

Favas *et al.* (Favas et al., 2012) studied the stream waters inside the mine influence at the Adoria mine area (Northern Portugal) and principal component analysis (PCA) showed a clear separation between AMD galleries and AMD tailings. The tailings had a greater level of contamination to the stream waters.

A case study in Sardinia, Italy, was conducted with a characterization plan to determine hazardous sources and contaminant pathways by assessing soil samples, stream sediment, fine grained ore-processing waste, surface water and groundwater (Cidu et al., 2012a).

The relationships between specific conductivity (SC) and dissolved elements were used to evaluate the metal load of the River Meca, a tributary of the Odiel, in Spain (Galvan et al., 2012). The relationships between the SC and the concentration of dissolved

elements were strong although some key elements such as Fe showed a very poor correlation. A simple methodology was used to elucidate their different behaviors.

A multivariate approach using nonlinear principal component analysis (Isomap) was used to identify the prevailing processes that controlled the water quality of the complex surface water system (Maassen et al., 2012). The first four principal components explained 79% of the variance in the dataset, indicating anthropogenic impact factors, such as groundwater from degraded peat areas and the influence of coal mining drainage with respect to SO₄. Isomap was a very powerful tool for gaining a better insight into the dominating processes of the surface water quality.

The chromium reducible sulfur (CRS) method was examined to measuring forms of sulfur commonly found in mine waste materials (Schumann et al., 2012). By comparison of acid base account (ABA) values for a number of coal waste samples, it was demonstrated acidity predicted from CRS analysis had much a better agreement with actual acidity than total S analysis.

Factor analysis was performed on the surface water and sediment quality related to AMD producing from an abandoned sulfide mine in Smolnik (Slovak Republic) (Singovszka and Balintov, 2012). Multivariate statistical analysis for evaluation and interpretation of the data proved to be valuable in stimulating better policy and decision-making for environmental management.

New Techniques. The use of zinc (Zn) isotopes was evaluated to complement traditional geochemical tools

in the investigation of contaminated waters at the former Waldorf mining site in the Rocky Mountains, Colorado, U.S.A. ([Aranda et al., 2012](#)). Zinc isotope analysis proved useful and it could be improved considerably with the addition of a comprehensive experimental foundation to interpret the complex isotopic relationships found in soil pore waters.

A support vector machine (SVM) was used to predict the heavy metals in AMD and the obtained results were compared with those of the general regression neural network (GRNN) ([Aryafar et al., 2012](#)). The SVM could be an easy and cost-effective method to monitor groundwater and surface water impacted by AMD.

[Graupner et al., \(2012\)](#) developed a process oriented methodology to determine the geochemical composition of dump bodies on the base of geological and geochemical data from pre-mining exploration. It showed that geological data resolution was less significant compared to geochemical data. Furthermore, the usage of average geochemical properties seemed to be insufficient if the methodology was applied to large mining districts.

[Canovas et al. \(2012\)](#) investigated the comprehension of interactions between AMD sources, freshwaters, particulate matter and sediments. A methodology to quantify the proportions of different contributing sources was proposed. The method was based on the mass balance of solutes and accounted for the uncertainty of end-members.

The MiniSipper, a new water sampler, was studied for long-duration, high-resolution water sampling in remote areas ([Chapin and Todd, 2012](#)). MiniSippers were deployed to evaluate AMD inputs from the Pennsylvania Mine to the Snake River watershed in Summit County, CO, U.S.A. MiniSipper metal results agreed within 10% of EPA-USGS hand collected grab sample results.

A strontium (Sr) isotope was used to identify and quantify the interaction of Marcellus Formation produced waters with other waters in the Appalachian Basin in the event of an accidental release, and to provide information about the source of the dissolved solids ([Chapman et al., 2012](#)). Sr isotope ratios could be used to sensitively differentiate between Marcellus Formation produced water and other potential sources of TDS into ground or surface waters([Chapman et al., 2012](#)).

A new set of water level monitoring systems which could cover the entire coal mine working environment was developed ([Jin et al., 2012](#)). The CAN bus communication was used to communicate among devices, which greatly improved the accuracy rate of data transmission suitable for field use.

[Lghoul et al. \(2012b\)](#) used electrical resistivity tomography (ERT) and seismic refraction data at the Kettara mine site, north-northwest of Marrakech, Morocco, to determine the nature of the geological substrate of the tailings pond and to investigate the pollution zones associated with sulphide waste dumps. It

was found that the results from ERT and seismic refraction were complementary.

Rapantová *et al.* (2012) developed a method to quantify the different sources of water entering a mine, based on the hydrochemical nature of the waters from individual aquifers that contributed to the mine water mixture. Water quality was mainly influenced by geochemical reactions of waters in contact with the atmosphere and the reverse dissolution of the accumulated precipitates in the open pit areas.

Hyperspectral low spatial resolution was used to map mine waste from massive sulfide ore deposits, mostly abandoned, on the Iberian Pyrite Belt (Riaza *et al.*, 2012b). Hyperspectral data were found invaluable in giving quick hints on the quality of the rapidly changing state of the contamination generated by sulfide mine waste, enabling the authorities to activate mitigation procedures.

In situ and time-resolved quick-scanning X-ray absorption spectroscopy and X-ray diffraction were used to study the phases and stability of ferric iron products formed early during neutralization of AMD waters formed between 4 min and 1 h when ferric iron sulfate solutions were partially neutralized by addition of NaHCO_3 ($[\text{HCO}_3^-]/[\text{Fe}^{3+}] < 3$) (Zhu *et al.*, 2012). This work provided new insight into the formation, stability and reactivity of some early products.

Protection, Prevention and Restoration

Passive Treatment. Iron (Fe) accumulation was characterized in periphytic mats across an Fe settlement

lagoon receiving mine drainage in Scotland, UK, between March and June 2008 (Letovsky *et al.*, 2012). The mean measured Fe accumulation rate by periphyton substrates was $0.021 \text{ gm}^{-2} \text{ day}^{-1}$ and exposure of large surface areas of periphyton substrate in the settlement lagoon would only increase the Fe removal efficiency of the lagoon by c.1%.

The surface application of waste glycerol (WG) to reduce release of AMD constituents from mine tailings was evaluated (Behrooz and Borden, 2012). Beneficial characteristics of the WG included high aqueous solubility, high organic content, and high alkalinity. Significant reductions in iron, sulfate, hot acidity, aluminum, copper, and manganese was obtained.

Microbial community analysis was conducted to evaluate the effectiveness of a passive flow sulfate reducing bioreactor to treat coal mine drainage (Burns *et al.*, 2012). The results of the study supported the use of passive flow bioreactors to lower the acidity, metal, and sulfate levels present in the AMD at the Tab-Simco mine. In the meanwhile, modifications of the system are necessary to both stimulate sulfate-reducing bacteria and inhibit sulfur-oxidizing bacteria for better performance.

Reactive transport simulations were conducted to evaluate possible effects of stratification on the potential of sulfide-bearing mine tailings to form protective cemented layers (Meima *et al.*, 2012). Stratification was found to play a crucial role in cemented layer formation. Cemented layers were absent or insignificant in systems

with a homogeneous distribution of Fe-bearing sulfides ([Meima et al., 2012](#)).

The behavior of the limestone drains at the Lorraine mine site in Quebec, Canada, was evaluated by the hydraulic residence time (HRT) using various tracer tests ([Maqsoud et al., 2012](#)). It was found the HRT in the Lorraine limestone drains was close to the minimum value targeted at the design stage but was significantly different than those estimated from the geometrical characteristics and porosity of the drains and the water flow discharge.

The influence of the carbonate rock mineralogy and their particle size on neutralizing capacity was examined in two different anoxic conditions: in batch reactors, and in columns having a hydraulic retention time of 15 h ([Genty et al., 2012b](#)). The neutralization capacity of calcite was more important than for dolomitic rock, and smaller particle size produced higher alkalinity. It was concluded anoxic limestone drain alone was not effective in treating high iron AMD.

Fenton *et al.* ([2012](#)) assessed the iron ochre, a by-product of AMD as a phosphorus (P) sequestration material. Quick and sustained metal release was observed, indicating it was not feasible for use as a soil amendment to control P release to a water body.

The impact of a lime doser on the chemistry and biological community was investigated in the Hewett Fork subwatershed ([Kruse et al., 2012](#)). There was little lasting change in the water chemistry with the doser offline for a two-week period. Surveys showed the fish community

was seriously impacted due to non-treatment while the macroinvertebrate community exhibited little impact.

The performance of an open limestone channel (OLC) was evaluated in improving the surface water quality of intermittent drainage from mine tailings deposits ([Alcolea et al., 2012](#)). Increased pH and alkalinity were observed while the EC, TS, K, Mg, SO_4^{2-} , Al, Mn, Fe, Ni, Cu, Zn, As, Cd, and Sb decreased downstream. It was concluded that OCL was effective to mitigate intermittent AMD in Mediterranean and semi-arid regions ([Alcolea et al., 2012](#)).

Lizama Allende *et al.* ([2012](#)) indicated that the most effective mechanism of arsenic removal in vertical flow wetlands was coprecipitation with iron. Alkaline wetland media, to increase the pH of the water, enhanced arsenic removal. Combinations of media might be needed in order to optimize the efficacy and sustainability of heavy metal removal.

Prevention and Containment. A two-stage flotation process was evaluated to reduce ARD potential before waste disposal by producing (i) a low-volume sulfide-rich concentrate, (ii) a high-volume benign (low sulfur) tailings, and (iii) a coal concentrate ([Kazadi Mbamba et al., 2012](#)). The results of acid generating potential tests (both static and biokinetic) indicated that a low-sulfur tailings had a low ARD potential.

The mitigation of AMD generation was evaluated by (1) sustained-release of bactericides and several passivators such as sodium triethylenetetramine-

bisdithiocarbamate, (2) absorbent materials from modified maize straw, peanut shells and rice straw capable of simultaneously removing heavy metals and sulfate ions, and (3) adoption of the economic crop of corn to remediate contaminated soils ([Dang et al., 2012](#)).

The mechanics of unsaturated flow and evaporation were studied in conjunction with the sensitivity of geo-environmental performance of sulfidic surface thickened tailings deposits to excessive evaporation due to increased potential for oxidation and AMD ([Dunmola, 2012](#)). There was a need to manage sulphidic tailings disposal operations so that both the geotechnical and geoenvironmental performance of the deposit are optimized.

He *et al.* ([2012](#)) designed a grout curtain based on computerized tomography in the key areas of the mine and groundwater level monitoring data, which was highly effective in reducing the groundwater levels in the Gaoyang Iron Mine area and amount of water pumped from the mine.

Dagenais *et al.* ([2012](#)) demonstrated that the modified oxygen consumption (MOC) test is an effective tool to assess the performance of oxygen barrier covers used to prevent AMD.

The potential of several surface coating agents to inhibit the oxidation of metal sulfide minerals was examined by conducting laboratory scale batch experiments and field tests ([Ji et al., 2012](#)). Six coating agents (KH_2PO_4 , MgO and KMnO_4 as chemical agents, and

apatite, cement and manganite as mineral agents) were studied. It was found that the use of surface coating agents was a promising alternative for sulfide oxidation inhibition at AMD sites.

Shimada *et al.* ([2012](#)) discussed acid generation mechanism and its control with cover systems and proposed a new covering strategy of multi-layer cover systems based on preliminary laboratory results.

Long term monitoring of the physical and chemical effects of using coal-combustion residues (CCRs), in particular fixated flue gas desulfurization (FGD) sludge, as a major component to abate AMD generation was conducted ([Naylor et al., 2012](#)). It was found that CCR cap and transient perching of groundwater above the cap effectively minimized water flow and significantly improved in the quality of groundwater on-site and surface water leaving the site. Strategic usage of coal-combustion residues in reclamation programs produced beneficial effects, including acid drainage reductions.

Thakur Jha *et al.* ([2012](#)) proposed a method using carrier-microencapsulation (CME) using Si-catechol complex - for preventing pyrite oxidation. The CME coating was very effective even at low concentrations of 1 and 5 mol m^{-3} . The amount of Fe and S leached were lower from the pyrite with CME treatment than without CME treatment, indicating the suppression of pyrite oxidation.

Complete metal removal from highly-polluted AMD was achieved by the use of a pilot multi-step passive remediation system, i.e., a limestone-based passive remediation technology followed by a novel reactive

substrate (caustic magnesia powder dispersed in a wood shavings matrix) ([Macias et al., 2012b](#)). This MgO-step was effective in reducing high concentrations of Zn along with Mn, Cd, Co and Ni below the recommended limits for drinking waters.

Spent mushroom compost (SMC) was assessed as a reactor matrix in a passive bioreactor involving sulfate reducing bacteria (SRB) for AMD treatment ([Das et al., 2012](#)). Removal of iron and sulfate from influent was over 77 and 90%, respectively, for first 13 weeks, while sulfate removal efficiency suddenly dropped down to 31% thereafter due to low dissolved organic carbon (DOC) values.

Toxicity Assessment

The toxicity of synthetic AMD to activated sludge microbes was evaluated using oxygen uptake rate (OUR) inhibition tests, which showed that activated sludge can withstand high proportions of AMD (EC50 19–52% AMD by volume) ([Hughes and Gray, 2012](#)). The acclimatized activated sludge microbial community was able to adapt to AMD sufficiently so that shock loads of metals and acidity did not significantly inhibit OUR.

Adaptive microevolution with regard to increased metals tolerance was investigated ([Saro et al., 2012](#)). Clonal lineages of *Daphnia longispina* did not acclimate to metals during a long-term sublethal exposure. There was no correlation between lethal and sublethal responses in the *Daphnia longispina*. Resistance to metals at sublethal level

of Cu was found to correlate to lower intrinsic growth rates under control conditions.

The toxicity of effluent from three AMD treatment plants in Korea was monitored from August 2009 to April 2010 using *Daphnia magna* (reference species) and *Moina macrocopa* (indigenous species) ([Seo et al., 2012](#)). Acute lethal toxicity was observed in the Samma effluent due to incomplete neutralization of AMDs by the successive alkalinity producing system (SAPS). There was no significant difference in toxicity values (TU) between *D. magna* and *M. macrocopa* ($p < 0.05$).

A study of the Ely Creek watershed (Lee County, Virginia) indicated that passive remediation techniques had a positive effect on ecological recovery downstream of remediated AMD seeps ([Simon et al., 2012](#)). At the site most impacted by AMD, mean pH was 2.93 and improved to 7.14 after remediation. An ecotoxicological rating system was developed which combined ten biotic and abiotic parameters. The system showed improvement in the watershed after remediation.

The influence of dissolved organic carbon (DOC) on the toxicity of aluminum (Al) at pH 5, to the tropical green hydra (*Hydra viridissima*), green alga (*Chlorella sp.*), and cladoceran (*Moinodaphnia macleayi*) was assessed ([Trenfield et al., 2012](#)). Two DOC sources were used: soft billabong water (SBW) and Suwannee River fulvic acid (SRFA) standard. The toxicity of dissolved Al was up to six times lower using 10mgL⁻¹ DOC (in the form of SRFA), relative to toxicity observed at 1mgL⁻¹ DOC. The increased ability of SRFA in reducing

Al toxicity was due to its greater affinity for complexing Al.

The potential hazard posed by the mining effluents to freshwater communities in Bracal and Palhal, Portugal, was studied ([Vidal et al., 2012](#)). Short- and long-term ecotoxicological tests were performed on elutriates from river sediments collected at each site using standard test organisms that cover different functional levels (*Vibrio fischeri*, *Pseudokirchneriella subcapitata*, *Lemna minor*, and *Daphnia sp.*). The elutriates from the sediments of Palhal were very toxic to all tested species, while those from Bracal showed generally no toxicity for the tested species. It was found that an ecotoxicological approach was very useful to help in the prioritization/scoring of the most critical areas impacted by deactivated mines.

Soybeans (*Glycine max*), cattails (*Typha latifolia*), goldenrods (*Solidago sp.*), and reed grass (*Phragmites australis*) were found growing at an AMD-impacted site contaminated with 9430 mg kg⁻¹ Al, 76,000 Fe mg kg⁻¹, ~150 mg kg⁻¹ Mn, and 420 mg kg⁻¹ Mg ([Cutright et al., 2012](#)). The metal uptake selectivity was Fe>>Mg~Mn>Al for cattails, Mg>Mn>Fe>Al for goldenrods, and Fe>>Al>Mg>Mn for reeds. It was found that cattails and reeds were more effective at the site than the soybeans or goldenrods in contaminate uptake.

Biological Characterization

Microbial Communities. When domestic wastewater was used as a carbon source for AMD treatment, dominant species in the bioreactor were

fermentative (*Clostridium spp.*, *Delftia spp.*, *Paludibacter spp.* and *Pelotomaculum spp.*) and sulfate-reducing bacteria (*Desulfomonile spp.*, *Desulfovibrio spp.*, *Desulfosporosinus spp.* and *Desulfotomaculum spp.*) ([Sanchez-Andrea et al., 2012b](#)).

The response of *Euglena mutabilis* and *Euglena gracilis* to arsenic metalloid was studied in an AMD environment ([Halter et al., 2012](#)). *E. mutabilis* showed highly hydrophobic cell surface properties and a higher tolerance to water-soluble arsenical compounds but not to hydrophobic ones.

Quantification of a microbial population in Tinto River sediment, Spain, demonstrated that bacteria (98%) dominated over archaea (2%) and important differences were detected at the class and genus levels, reflecting differences in pH, redox potential, and heavy metal concentrations ([Sanchez-Andrea et al., 2012a](#)). In layers where sulfate-reducing bacteria were abundant, pH was higher and redox potential and levels of dissolved metals and iron were lower, indicating the attenuation of AMD characteristics.

Justice *et al.* ([2012](#)) reported a transition from bacteria- to archaea-dominated communities in microbial biofilms sampled from the Richmond Mine AMD system (~pH 1.0, ~38C) and in laboratory-cultivated biofilms. The archaea were from the class *Thermoplasmata*, and in some cases, the highly divergent ARMAN nanoarchaeal lineage. Laboratory cultivation experiments demonstrated anaerobic enrichment of *Ferroplasma* and *Aplasma* coupled to the reduction of ferric iron.

Community and diet analysis in 20 streams in New Zealand demonstrated that mining streams receiving anthropogenic inputs of acidic and metal-rich drainage had much simpler food webs (fewer species, shorter food chains, less links) ([Hogsden and Harding, 2012](#)).

It was also found that elevated metal concentrations, regardless of source, played a more important role than acidity in driving food web structure.

Biomass and metabolism of epilithic communities were used as an indicator of impact and recovery in streams affected by AMD and remediated by passive treatment systems ([DeNicola et al., 2012](#)). It indicated that changes in food web structure due to AMD stress had less effect on epilithic productivity than environmental conditions within the stream.

Microbial Oxidation. Huang and Zhou ([2012](#)) studied the processes of secondary iron hydroxysulfate mineral formation where the Fe^{2+} ion was oxidized by the following three methods: (1) bio-oxidation treatment by *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*); (2) rapid abiotic oxidation of Fe^{2+} with H_2O_2 (rapid oxidation treatment); (3) slow abiotic oxidation of Fe^{2+} with H_2O_2 (slow oxidation treatment). Fe^{2+} oxidation rate greatly affected the mineral phase of precipitates, and slow oxidation of Fe^{2+} was helpful in improving jarosite formation.

Jarosite immobilization of *acidithiobacillus ferrooxidans* was investigated for the iron removal performance of simultaneous bio-oxidation and precipitation ([Wang and Zhou, 2012](#)). The increase

in the amount of inoculated jarosite not only sped up Fe^{2+} oxidation, but also improved the efficiency of Fe^{3+} removal, thereby facilitating the removal of iron from acidic, ferrous- and sulfate-rich solutions.

Luptakova *et al.* ([2012a](#)) monitored the occurrence of autochthonous chemolithotrophic Fe- and S-oxidizing bacteria of *Acidithiobacillus ferrooxidans* species in AMD from the selected sulfide mineral deposits and their waste deposits on the territory of Slovak Republic.

Sulfate and Iron Reduction. Food waste-based compost and zeolite was used to examine the feasibility for AMD treatment ([Hwang et al., 2012](#)). Black-colored precipitates were observed indicating the formation of metal biosulfides by sulfate-reducing bacteria (SRB). Microbial and molecular analyses revealed that several species of heterotrophic bacteria (SRB and iron-reducing bacteria) were present in the bioreactors where Microbial consortium, such as SRB species (*Desulfotomaculum putei*), and cellulosic-degrader (*Ruminococcus sp.*) were identified.

A bench-scale upflow anaerobic sludge blanket (UASB) reactor supplemented with ethanol as an external carbon source was used for AMD treatment ([Rodriguez et al., 2012](#)). The inoculum of the reactor was the anaerobic granular sludge from poultry slaughterhouse wastewater. The complete oxidation of the ethanol was the dominant path for the reduction of sulfate.

Simultaneous reduction of structural Fe(III) and aqueous As(V) was observed during the dissolution of synthetic Pb-As jarosite ($\text{PbFe}_3(\text{SO}_4, \text{AsO}_4)_2(\text{OH})_6$) by

Shewanella putrefaciens using batch experiments under anaerobic circumneutral conditions (Smeaton et al., 2012). The structural Fe(III) reduction was thermodynamically driven while aqueous As(V) reduction was triggered by detoxification induced to offset the high As(V).

An acid-tolerant, Fe(III) and sulfate-reducing bacterium, *Desulfosporosinus* sp. strain GBSRB4.2 affected the mineralogical transformations of Fe phases under geochemical conditions associated with AMD-impacted systems (Bertel et al., 2012). In media that contained abundant Fe(III), the activities of strain GBSRB4.2 enhanced the transformation of schwertmannite to goethite (-FeOOH), due to the increased pH and Fe(II) concentrations that resulted from the activities of GBSRB4.2.

Macroinvertebrate and Plant Characterization.

The concept of assemblage tolerance profiles (ATPs) was used to estimate the tolerances for pH and dissolved oxygen (DO) of common families of macroinvertebrates in rivers in south-eastern Australia (Chessman and McEvoy, 2012). It was found that sites with more exposure to mine drainage would have ATPs indicating greater tolerance to low pH, whereas sites with more exposure to sewage discharges would have ATPs indicating greater tolerance of low DO.

Lipid analysis of benthic and floating biofilms from an AMD site in western Indiana was conducted (Dasgupta et al., 2012). The dominance of

photosynthetic organisms, mainly *Euglena*, was found as indicated by the detection of abundant phytadiene, phytol, phytanol, polyunsaturated n-alkenes, polyunsaturated fatty acids, short-chain (C25-32) wax esters (WE), ergosterol, and tocopherols.

Metal uptake selectivity was studied for four plant species found naturally growing at an AMD impacted site, including soybeans (*Glycine max*), cattails (*Typha latifolia*), goldenrods (*Solidago* sp.), and reed grass (*Phragmites australis*) (Cutright et al., 2012).

Cattails and reeds were more effective than the soybeans or goldenrods when metal translocation factors, shoot concentrations, and toxicity of the contaminants were correlated.

Fate and Transport

Arsenic. Trace element concentrations in soil, sediments, and waters in the vicinity of the Geita Gold Mines and North Mara Gold Mines in northwest Tanzania, Central Mexico, were studied to understand the impact of AMD (Almas and Manoko, 2012). In particular, As concentration was more than one order of magnitude higher than the WHO drinking water recommendations.

The mobility of arsenic around mining districts was studied using synthetic biotic and abiotic schwertmannite types (Paikaray and Peiffer, 2012b). It was found that schwertmannites could be used as potential adsorbents for arsenite immobilization where the total uptake was controlled by both ion exchange and surface precipitation.

The uptake of arsenate, chromate and molybdate by synthetic schwertmannite was studied to understand the mobility and availability of contaminants in soils and waters affected by AMD ([Antelo et al., 2012](#)). It was observed that different adsorption mechanisms were involved for the three oxyanions (surface complexes and anion exchange).

Interaction between arsenic and uranium was investigated to understand uranium mobility in aqueous solutions such as AMD ([Gezahegne et al., 2012](#)). It was found that the bidentate arsenates were bound to uranium with one of the binding oxygen atoms being protonated. $\text{UO}_2\text{H}_2\text{AsO}_4^+$, and $\text{UO}_2(\text{H}_2\text{AsO}_4)_2^0$ were important species in acidic uranium-arsenic-rich solutions.

The sources and behavior of arsenic and trace elements in groundwater and surface water was investigated in the Poopo Lake Basin, Bolivian Altiplano, which was impacted by AMD ([Ramos Ramos et al., 2012](#)). It was concluded that the mobility of As and other trace metals in the region was due to: (a) weathering of sulfide minerals, (b) oxidation of pyrite and/or arsenopyrite in mineralized areas and (c) desorption from hydrous ferric oxide (HFO) surfaces.

Paikaray *et al.* ([2012](#)) studied the As(III) mobility in schwertmannite precipitated in acid mine impacted areas by assessment of the interaction, redox conditions and schwertmannite metastability. Schwertmannite produced by a biotic process had a rapid As(III) uptake followed by slow retention where Ionic exchange governed the total As(III) uptake. Redox

instability of sorbed As(III) occurred at an extremely high Fe(III):As(III) ratio (5.5×10^5) leading to surface oxidation to As(V).

The mobility of As was examined in two mine tailings in the Kemerovo and Cheljabinsk regions in Russia ([Yurkevich et al., 2012](#)). The potential of natural materials to attenuate As dispersion in the broader environment was also evaluated. The main minerals of As in tailings were arsenopyrite (FeAsS) and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). High As levels were in the drainage and in the adjacent rivers. High As was also observed in the sediments of the affected rivers 100m downstream, indicating a source of river water contamination. As mobility were reduced by the formation of sulfides and arsenides in the pond and wetland sediments ([Yurkevich et al., 2012](#)).

Arsenic species mobility was evaluated with dissolved and particulate metals along a stream affected by AMD in the Iberian Pyrite Belt (SW Spain) ([Sarmiento et al., 2012](#)). Dissolved metals were higher during the dry season and increased progressively along the water course. Total As increased downstream while the $\text{As}^{3+}/\text{As}^{5+}$ ratio decreased. The same pattern was observed for both $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{As}^{3+}/\text{As}^{5+}$ ratios. In the particulate phase, As was associated with the Fe minerals while Pb was associated with the clay colloids.

The fate of As(III) pre-adsorbed to bio-synthesized schwertmannite (SHM) was investigated because SHM precipitated from AMD often contained high levels of As(III) ([Paikaray and Peiffer, 2012a](#)).

Significant As release was detected during the initial phase of the transformation of As-containing SHM, which was rapidly re-adsorbed, probably to the new phase.

Chen and Jiang (2012) investigated the water chemistry and mineralogy of the precipitates in the water fall and creek sections of the AMD in Chinkuashih area, Taiwan, and found that the precipitation of schwertmannite were associated with removal of metals and As. The water fall section showed high ferrous oxidation rate and high As adsorption rates.

Rare Earth Elements (REEs). REEs were studied in the sediments of salt marshes from the Guadiana Estuary, SW Iberian Pyrite Belt (Delgado et al., 2012). REE patterns demonstrated acid-mixing processes between fluvial waters affected by AMD and seawater. REE distributions in the mouth (closer to the coastal area) indicated slightly Light REE-enriched and flat patterns.

REEs as well as Sc, Y, and U were examined in the water of an affected AMD system (Borrego et al., 2012). Significant dissolved concentrations of the target elements were observed in the fluvial sector of this estuary system (Sc 31 g L⁻¹, Y 187 g L⁻¹, U 41 g L⁻¹, S rare earth elements 621 g L⁻¹), with pH values below 2.7. The largest rare earth elements removal occurred in the medium-chlorinity zone.

The presence of REEs in AMD was investigated in the Sitai coal mine and the Malan coal mine in Shanxi province, China (Sun et al., 2012). AMD pH was the most important factor controlling the fractionation of REE.

The Fe, Al, and Mn colloids and secondary minerals also affected the fractionation. Speciation modeling indicated that sulfate complexes and free-metal species were the dominant REE species in the AMD.

Other Metals. The chemical fractionation and contamination intensities of trace elements were used to study the impact of AMD in streams in the Sarcheshmeh mine, southeastern Iran (Khorasanipour et al., 2012). It was found that As, Cu, Cd, Mo, Pb, Sb, Se, S, and Zn were highly concentrated in the contaminated sediments. The contaminants were found to be adsorbed and co-precipitated with amorphous Fe-oxides and carbonate phases.

To evaluate the mobility and bioavailability of the trace elements, a modified BCR sequential extraction method was studied in Huelva Township, SW Iberian Peninsula (Guillen et al., 2012). The mobility sequence was: Cu (82.01%)>Zn (71.14%)>Cd (68.35%)>Ni (50.44%)>Pb (36.39%)>Cr (29.22%)>As (18.82%).

Andra et al. (2012) reported the environmental hazards associated heavy metals at the L'ubietova Cu deposit (Slovakia), whose fate and transport depended on geochemical behavior of these elements. The mine drainage posed the most health risk because of its radioactivity and its high Fe, Cu, Cd and Pb contents. Speciation of As and Sb were As³⁺ and Sb³⁺ as well as the less toxic As⁵⁺ and Sb⁵⁺ species. Calculation of the acidity and neutralization potential indicated that the potential of the AMD water formation was limited.

Sb speciation was studied in the sediments along the drainage of the Upper Peter adit at the Bralorne Au mine in southern British Columbia, Canada (Beauchemin et al., 2012). Speciation analyses indicated that the sediments in the main pool accounted for around 70% of total Sb at the far end of the adit. Significant oxidation of the primary sulfides occurred inside the adit. Secondary Sb species as the result of the sulfide oxidation were most likely sorbed/co-precipitated with Fe³⁺, Mn³⁺, and Al-oxyhydroxides with the Fe as the dominant sink for Sb (Beauchemin et al., 2012).

To determine the processes that influenced the mobility of Fe, Zn, Cu, Ni, Cd, As, Sb, Cr and Tl in an As-rich base metal waste pile with abundant calcite in Zimapan, Central Mexico, the geochemistry and mineralogy of samples collected along depth profiles from an As-rich tailing deposit were studied (Armienta et al., 2012). Total concentrations decreased as: Fe>As>Zn> Pb>Cu>Sb>Cd>Cr>Ni>Tl. Mobility decreased as: Tl>Cd, Zn, Cu, Sb, Ni, As>Fe, Pb>Cr. The calcite present in the waste pile impacted the metal speciation, neutralized AMD, and reduced the mobility of most toxic metals and metalloids (TMMs).

Transport. Sediment and water mapping through hyperspectral Hymap data was investigated in the Odiel River (Huelva, southwest Spain), which was impacted by acidic water originated from mine waste piles of sulphide ore deposits (Riaza et al., 2012a). The mapping data identified the river locations key in tracing future significant contaminant fluctuations.

Kobylin *et al.* (2012) developed a thermodynamic model to generate a consistent set of values for the solubility of iron sulphate in a wide temperature and concentration range, which could be used to predict the mobility of metals in AMD.

Sloot and Zomeren (2012) developed a pH dependent leaching test (CEN/TS 14429) and a percolation leaching test (CEN/TS 14405) to characterize the release behavior of different sulfidic mining wastes. Mineral transformations on the surface of waste rock or tailings particles dictated metal release.

The sediment pollution index (SPI) and enrichment factor was used to study trace metal occurrence and mobility in streams near the Sungun Porphyry Copper Deposit in Northwest Iran (Moore and Aghazadeh, 2012). It was found that cadmium is the only element with a high potential for mobility and bioavailability in the sediments.

The role of iron colloids in copper speciation during neutralization was studied in a coastal creek impacted by AMD discharging to the Kwangyang Bay of South Korea (Jung et al., 2012). VMINTEQ modeling indicated that Cu speciation was dominated by interaction with Fe colloids during neutralization in a typical AMD.

The heavy metals and radionuclides from the AMD and discharge from phosphogypsum (PG) piles in the watershed of the Tinto and Odiel Rivers in Southwest Spain resulted in a significant impact on the estuary ecosystem (Hierro et al., 2012). The suspension of

benthic sediments led to the desorption of some of the radionuclides, making them bioavailable.

Transport of heavy metals from AMD was investigated in single, binary and multi-metal systems through lateritic soil columns which was modeled with the HYDRUS-1D using a local equilibrium convection-dispersion (CDeq) model, or chemical non-equilibrium two-site model (TSM) with first order kinetics (Chotpantarat et al., 2012). The TSM model indicated the highest sorption affinity of Pb^{2+} was under both binary and multi-metal systems and diffusion probably dominated the sorption and transport of heavy metals in the system.

Molson *et al.* (2012) developed a numerical model to study the transport behavior and geochemical evolution of AMD in discretely fractured porous media. The numerical model included groundwater flow, AMD infiltration, multi-component advective-dispersive transport, equilibrium geochemical speciation and water-rock pH-buffering reactions within a discrete fracture network (DFN).

The pollution of heavy metals was investigated in a catchment of the Matylda stream affected by an abandoned lead and zinc ore mine in Upper Silesia, southern Poland (Aleksander-Kwaterczak and Ciszewski, 2012). It was found that the ditches were a sink for zinc, cadmium and lead in permanently dry reaches, or transition zones in reaches with surface water flowing periodically. The metal concentrations and

distribution in the soil and groundwater demonstrated the slow mobilization of heavy metals in the valley bottom.

The metal distribution between water and sediment in the Smolnik Creek was studied in the Smolnik Cu-Fe deposit, Slovak Republic(Balintova et al., 2012c). The pH of the mine waters was 3.7-4.1, containing high concentrations of sulphates, Fe, Mn, Cu, Zn and Al. The resulted pH increase, due to mixing with surface water, led to the precipitation of metals and their accumulation in sediment.

Geochemical processes were studied to evaluate the metal partitioning in sediments and mineralogical controls on the AMD in Ribeira da agua Forte (Aljustrel, Iberian Pyrite Belt, Southern Portugal) (Maia et al., 2012). The coupled interplay of dissolution and precipitation of the secondary minerals (hydroxides and sulfates) was responsible for the low pH, between 3.9 and 4.5, along the stream. Schwertmannite precipitation and decomposition sustained the stream water pH at those levels. Other metals bound to oxyhydroxides were on the order of 60-70% for Pb, 50% for Cu and 30-60% for Zn.

Specific conductivity (SC) and dissolved elements were used to calculate the metal load of the River Meca, a tributary of the Odiel (SW Spain) (Galvan et al., 2012). A simple methodology based on the MIX code was used to elucidate the relationships between the SC and the concentration of dissolved elements. During the dry period, the precipitation of Fe-oxihydroxides reduced the concentrations of Fe, As, Cr, Pb and Cu. It was found

that SC alone was not sufficient to predict the dissolved metal loads in Mediterranean AMD streams.

Treatment Technologies

Neutralization. AMD is typically treated by neutralization with alkaline materials and the treatment can continue for many years. Predicting future AMD characteristics and appropriate treatment options is very challenging. Based on geochemical modeling, a predictive model was developed for AMD composition and the neutralization process ([Koide et al., 2012](#)). Estimations were made for two abandoned mines in Japan (a sulfur mine and a copper and iron mine) for AMD composition, neutralizer requirements, and sludge generation. The results indicated that the model effectively predicted AMD composition after termination of mining, improved the understanding of the lifecycle environmental costs in the mining industry.

Precipitated CaCO_3 compounds were recovered from pulped waste gypsum using some carbonate and hydroxide-based reagents and then used for AMD neutralization ([Zvimba et al., 2012](#)). CaCO_3 recovered from waste gypsum using Na_2CO_3 showed better results in significantly neutralizing AMD, compared with that recovered using $(\text{NH}_4)_2\text{CO}_3$ or $\text{NH}_4\text{OH}-\text{CO}_2$ or commercial CaCO_3 .

Steelmaking slag was converted to calcium carbonate (CaCO_3) using hydrochloric acid, ammonium hydroxide and carbon dioxide via a pH-swing process and the resulted calcium carbonate was used for the pre-

treatment of AMD from coal mines ([Mulopo et al., 2012a](#)). It was observed that the amount of hydrochloric acid and the CO_2 flow rate had a positive effect on the carbonation reaction rate. The CaCO_3 recovered from the reactor showed similar performance in AMD pre-treatment compared with the commercial CaCO_3 .

Cement kiln dust (CKD), a waste by-product, was evaluated to replace quicklime in the active treatment of acidic mine water ([Mackie and Walsh, 2012](#)). CKD was effective in achieving >97% removal of total zinc and iron. To achieve pH targets, CKD consumption was higher than quicklime, while CKD treatment generated a smaller volume of sludge.

The acidic pit Lake Bockwitz south of Leipzig (Germany) was treated, since 2004, with soda ash to meet water quality criteria for the lake effluent ([Ulrich et al., 2012](#)). Leaching of acidic sulfide mineral weathering products from the tertiary bank substrate was the dominant factor for the lake re-acidification. Process-based models were developed to reliably predict the water quality of mining pit lakes, which dictated the appropriate treatment measures and the requirements for cost-effective lake water conditioning.

Batch and long-term column experiments were conducted to investigate the secondary mineralogy and permeability variation during treatment of AMD using calcite as a neutralizing agent ([Liu et al., 2012](#)). Two coating layers on the calcite surface were found, with the internal layer as crystalline gypsum, and the external layer

is lepidocrocite, which gradually changed into goethite. The iron coating layer was a key factor of clogging during long-term treat leading to low bed permeability.

Apatite II, a biogenic hydroxyapatite (expressed as $\text{Ca}_5(\text{PO}_4)\text{OH}$) derived from fish bone, was used in batch and flow-through experiments to remove Pb^{2+} , Zn^{2+} , Mn^{2+} , and Cu^{2+} from mine drainage ([Oliva et al., 2012](#)). The fish-bone hydroxyapatite dissolution led to pH increase and removal of Pb^{2+} , Zn^{2+} , Mn^{2+} , and Cu^{2+} was by formation of phosphate-metal compounds on the Apatite II substrate, whereas removal of Cd^{2+} was by surface adsorption ([Oliva et al., 2012](#)).

A post audit for a reactive transport model was used to evaluate AMD treatment systems ([Runkel et al., 2012](#)). The model was able to accurately predict Al, As, Fe, H^+ , and Pb in dissolved concentrations in the treatment system, while the errors associated with Cd, Cu, and Zn are attributed to misspecification of sorbent mass of precipitated Fe.

Biological Processes. Food waste-based compost was evaluated in three bioreactors filled with mixtures of tailings, food waste-based compost, and zeolite ([Hwang et al., 2012](#)). Compared with the control, the leachate from two mixture-filled reactors showed high pH, low sulfate, and high metal removal. It was concluded that food waste-based compost could be promising for prevention of AMD generation and passive in situ treatment of pore water in weathered tailings.

Wood ash filters were used as a polishing step followed by sulphate reducing passive bioreactors (SRPBs) to treat AMD with high iron concentrations in five columns over 122 days ([Genty et al., 2012a](#)). It was demonstrated that the wood ash decreased iron concentrations for more than 100 days below 10 mg L^{-1} (99 % iron removal), mainly due to iron hydroxide precipitation and sorption.

A proton exchange membrane microbial fuel cell (MFC) was evaluated to increase the pH and remove Fe in the treatment of AMD dominated with iron ([Lefebvre et al., 2012](#)). At the cathode of the MFC, Fe^{3+} was reduced to Fe^{2+} , which is followed by Fe^{2+} re-oxidation and precipitation as oxy(hydroxi)des, and oxygen reduction and cation transfer to the cathode of the MFC further resulted in a rise in pH.

The performance of four substrates (manures, woodchips, millet fodders and sugarcane waste) was examined in sulfate reducing passive bioreactors for AMD treatment ([Choudhary and Sheoran, 2012](#)). The manures were effective in metals removal and pH increase, indicating that manures could be cost effective as a single substrate in passive treatment bioreactors.

Domestic wastewater (DW) was examined as a cost-effective carbon-source in biological sulfate reduction for the remediation of AMD ([Sanchez-Andrea et al., 2012b](#)). When DW was used, elevated removal of chemical oxygen demand (COD) (88%), sulfate (75%), Fe

(85%) and other dissolved metals (99% except for Mn) were achieved.

Mokone *et al.* (2012) examine the management of supersaturation and copper and zinc sulphide precipitation reactions in AMD remediation systems based on bacterial sulphate reduction. It was found that the extremely high supersaturation prevalent during metal sulphide precipitation was difficult to control using conventional approaches and the seeded fluidized bed reactor was not suitable for the application.

Matthies *et al.* (2012) studied the reducing and alkalinity producing systems (RAPS) to remediate net-acidic metalliferous mine drainage by creating anoxic conditions using bacterial sulfate reduction (BSR). Sulfur isotope data showed that sulfate in all mine waters had a common source, i.e., due to pyrite oxidation, while oxygen isotopes indicated that oxidation of pyritic sulfur is mediated by ferric iron in solution. It was found BSR was not as important as previously thought for metal removal in RAPS which had practical consequences for the design, treatment performance and long-term functionality of RAPS.

Castillo *et al.* (2012) conducted several experiments to evaluate zinc-tolerance of sulfate-reducing bacteria (SRB) for zinc mine drainage treatment. Sulfate was reduced to sulfide while Zinc concentrations also decreased to values below the detection limit. Meanwhile, the precipitation of newly-formed sphalerite and wurtzite, two polymorphs of ZnS, resulted in the formation of 2.5 nm-diameter spherical aggregates. The SRB-based zinc

removal step could completely reduce the mobility of metals in AMD impacted regions.

Compost-based biological systems were studied for the remediation of Zn contamination from a discharge in an abandoned metal mine and the effects of engineering scale on the reactor performance was investigated in a laboratory-scale column and a pilot-scale system (Gandy and Jarvis, 2012). The laboratory-scale column was more effective at removing zinc with approximately a 96 % reduction, while zinc removal was 84% in the pilot scale system.

A bench-scale upflow anaerobic sludge blanket (UASB) reactor with ethanol as an external carbon source was assessed in treating AMD from the Osamu Utsumi uranium mine (Caldas, MG, Brazil) through the biological reduction of sulfate (Rodriguez *et al.*, 2012). The predominant treatment mechanism in the reactor was the reduction of sulfate through complete oxidation of the ethano.

An anaerobic sulfidogenic reactor was evaluated in treating synthetic AMD containing Zn^{2+} , Cu^{2+} and Cd^{2+} , using rape straw as the carbon source (Wang *et al.*, 2012). The hydrolyzed cellulose and hemicellulose were the major components in the rape straw and the major mechanisms for the removal of heavy metals were adsorption and precipitation.

Continuous AMD treatment was examined using spent mushroom compost (SMC) as the reactor matrix in a passive bioreactor involving sulfate reducing bacteria

(SRB) ([Das et al., 2012](#)). SMC was mainly responsible for metal binding and provided the nutrients supply for the SRB.

A sulphate-reducing bacteria (SRB) reactor was used to produce biogenic iron sulfide, which was then used as a sorbent to remove heavy metals from waters with various zinc ions contents and mine drainage water samples from the Banska Stiavnica area (Slovakia) ([Jencarova and Luptakova, 2012](#)).

A novel modular bioremediation system was studied to facilitate the selective removal of soluble iron from mine-impacted water ([Hedrich and Johnson, 2012](#)). The system consisted of three modules: 1) rapid ferrous iron oxidation by the recently-characterized iron-oxidizing autotrophic acidophile, "*Ferrovum myxofaciens*", 2) controlled addition of sodium hydroxide to raise the water pH to 3.5 and to precipitate ferric iron as the mineral schwertmannite, and 3) a packed-bed bioreactor, inoculated with "*Fv. Myxofaciens*," acted as a polishing reactor, lowering soluble iron concentrations in the processed water to 1mg/L.

The long term performance of an AMD treatment bioreactor using chemolithoautotrophic sulfate reduction (CSR) was evaluated for groundwater remediation ([Bilek and Wagner, 2012](#)). It was observed that a constant biomass content and sulfate reduction rate of 0.25-0.30mmol SO₄/(Lh) was established after 1.3 years of operation.

Laboratory incubation experiments were conducted to examine the Mn(II) removal from coal mine drainage via oxidative precipitation of Mn(III/IV) oxides catalyzed by Mn(II)-oxidizing microbes and Mn oxide (MnOx) surfaces in oxic limestone beds ([Luan et al., 2012](#)). It was recommended to include MnOx-coated limestone and associated biomass from an operating bed as "seed" material when constructing new Mn(II)-removal beds.

Adsorption Processes. Sludge-derived biochar (SDBC) was evaluated to determine the adsorption and mechanisms of Pb removal from AMD ([Lu et al., 2012a](#)). It was found that Pb sorption primarily involved the coordination with organic hydroxyl and carboxyl functional groups as well as the co-precipitation or complex on mineral surfaces, indicating the application of SDBC could be a feasible strategy for removing metal contaminants from AMD.

Four types of natural and synthetic sorbents were examined for Fe, Cu, Al, Mn and Zn removal from AMD in Smolnik, Slovakia ([Balintova et al., 2012b](#)). The turf brush sorbent Peatsorb had satisfactory results for the removal of metals at a pH below 4.

The gangue minerals from mineral processing were used as cheap adsorbents to remove phenol from mine drainage ([Jabonska, 2012](#)). It was found that the most effective gangue mineral was claystone while mudstone was the least effective. For an initial phenol concentration of 10 mg/L, 50% removal was achieved.

Activated carbon was used to remove mercury from drainages from coal mines in Guacheta, Colombia (Rojas et al., 2012). The breakthrough curves using the Bohart and Adams model was studied and the model allowed the design and optimization of the performance of fixed bed adsorption systems for the removal of Hg^{2+} ions.

An adsorption process was used to treat AMD in the Slovak Republic, where the turf brush PEATSORB and zeolite were employed for Fe, Cu and Zn removal (Balintova et al., 2012a). The effects of different parameters (ion concentration, pH) on sorption efficiency and the removal mechanism of Fe, Cu and Zn were evaluated.

Bentonite clay was used as an adsorbent to recover rare earth elements from AMD in South Africa (Van Der Watt and Waanders, 2012). After adsorption, acid leaching was employed to selectively remove neodymium, samarium, and dysprosium as a group from other metals in the bentonite clay.

Clinoptilolite, a natural sorbent, was employed to remove zinc from ARD in a slurry bubble column and the exhausted sorbent could be regenerated with NaCl solution at pH 3 (Xu et al., 2012).

AMD sludge rich in Fe and Al oxides was evaluated as an economical adsorption media for the removal of P from wastewaters in fixed bed sorption systems (Sibrell and Tucker, 2012). A relatively small media particle size (average particle radius 0.028 cm) resulted in 96 % removal of P from the influent over 46 days of continuous operation, indicating that fixed bed

sorption of P would be a feasible option for the beneficial utilization of AMD residues.

Sulfate Removal. Mulopo *et al.* (2012b)

investigated the batch regeneration of barium carbonate (BaCO_3) from barium sulphide (BaS) slurries by passing CO_2 gas into a pilot-scale bubbling column reactor in the alkali barium calcium (ABC) desalination process. The recovered BaCO_3 was then used for sulphate removal from high sulphate AMD. The CO_2 flow rate had a significant effect on the carbonation reaction rate for BaCO_3 regeneration and BaCO_3 morphology in a bubbling column reactor. The obtained BaCO_3 was effective in sulphate removal for AMD treatment compared with commercial BaCO_3 .

Barium salts were used following the lime neutralization of AMD treatment to further reduce the sulphate concentration to acceptable levels (Swanepoel et al., 2012). The reactor temperature, initial sulphate concentration, and molar ratio of barium to sulphate had significant impact on sulphate removal.

Sulfate removal from neutral mine drainages was achieved using limestone because calcium ions on the solid surface could bind sulfate ions (Silva et al., 2012a). The continuous stirred-tank experiments demonstrated a sulfate concentration reduction from 588.0mg/L to 87.0mg/L at a 210-min residence time. Sulfate removal by limestone was modeled by the Langmuir isotherm with a maximum loading of 23.7mg/g. Sulfate removal with limestone seemed to be effective in treating mine waters with sulfate concentrations of 1200-2000 mg/L.

Metal Recovery. Compared to typical AMD neutralization, a selective precipitation/photoreduction combined process was developed to produce magnetite from the iron present in AMD ([Silva et al., 2012b](#)).

The selective precipitation of iron as a ferric hydroxide was followed by the dissolution of iron with sulfuric acid and the photoreduction of Fe^{3+} to Fe^{2+} . Then, the ferric/ferrous solution was used to produce magnetite, indicating that sludge waste issues were mitigated by a valuable mineral.

[Lu et al. \(2012b\)](#) studied the recovery of Cu and Zn from acidic mine drainage during bioremediation using straw bioremediation system, where > 97.0% of Cu and > 87.0% of Zn were recovered. Low pH could severely decrease the recovery rate of Zn, while it had no influence on that of Cu. Selective metal recovery might be achieved with relatively short HRT and bioreactor process optimization.

[MacIngova and Luptakova \(2012\)](#) reported the results of studies conducted to develop and optimize the process of selective sequential precipitation (SSP) of selected metals (Fe, Cu, Al, Zn, Mn) to produce high recoveries of metals from AMD. Subsequently, biological system utilized hydrogen sulphide produced by sulphate-reducing bacteria to precipitate metals as sulfides at the various values of AMD pH.

Other Processes. To treat acidic drainage from a Pb-Zn mine containing high levels of heavy metals, coal-mine drainage sludge (CMDS) was examined in a pilot-scale system consisting of a stirring tank reactor, settling tank, and sand filter ([Cui et al., 2012](#)). CMDS

effectively neutralized the acidic drainage due to its high alkalinity production and the calcite and goethite contained in CMDS contributed to dissolutive coprecipitation and complexation with heavy metals.

A pretreatment via pH adjustment with CaO followed by electrocoagulation using iron and aluminum electrode sets was used to treat the AMD accumulated in the "Robule" Lake, the part of the Bor copper mining and smelting complex in Serbia ([Orescanin and Kollar, 2012](#)). The system was proven efficient with the following % removal: EC = 55.48%, SO_4^{2-} = 70.83%, Hg = 98.36%, Pb = 97.50%, V = 98.43%, Cr = 99.86%, Mn = 97.96%, Fe = 100.00%, Co = 99.96%, Ni = 99.78%, Cu=99.99% and Zn=99.94%.

To pre-treat turbid coal mine drainage, a filtration system free of chemical agent additives was investigated at different aperture sizes and rotation speed. The separated slime can be directly reused as a fuel ([Zhang et al., 2012](#)).

The mine drainage from the Eshydia phosphate mine in southern Jordan was treated by dissolved air flotation (DAF) with a commercial flocculant and subsequent nanofiltration (NF) ([Al-Zoubi and Al-Thyabat, 2012](#)). DAF effectively removed 50 % of the suspended solids and total dissolved solids (TDS) and the treated water was eligible for reuse in the phosphate mine or for irrigation.

Schwertmannite, a mineral found in AMD, was studied for the photoreduction of Cr(VI) by small

molecular weight organic acids (SOAs) (Jiang et al., 2012). It was found the addition of schwertmannite significantly enhanced the reduction of Cr(VI) by SOAs.

The feasibility of heavy metals removal from AMD in the Tunel Kingsmill outlet of the Rio Yauli (district of Yauli - Peru) was demonstrated using electrowinning followed by selective sequential precipitation of metals with H₂S produced by sulfate-reducing bacteria (Luptakova et al., 2012b). The electrowinning achieved about 95 - 97% Zn and Mn removal (as MnO₂) with a relatively low energetic consumption. The selective sequential precipitation process removed metals (Fe, As, and Al) with 97 - 99% efficiency as metal sulfides.

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