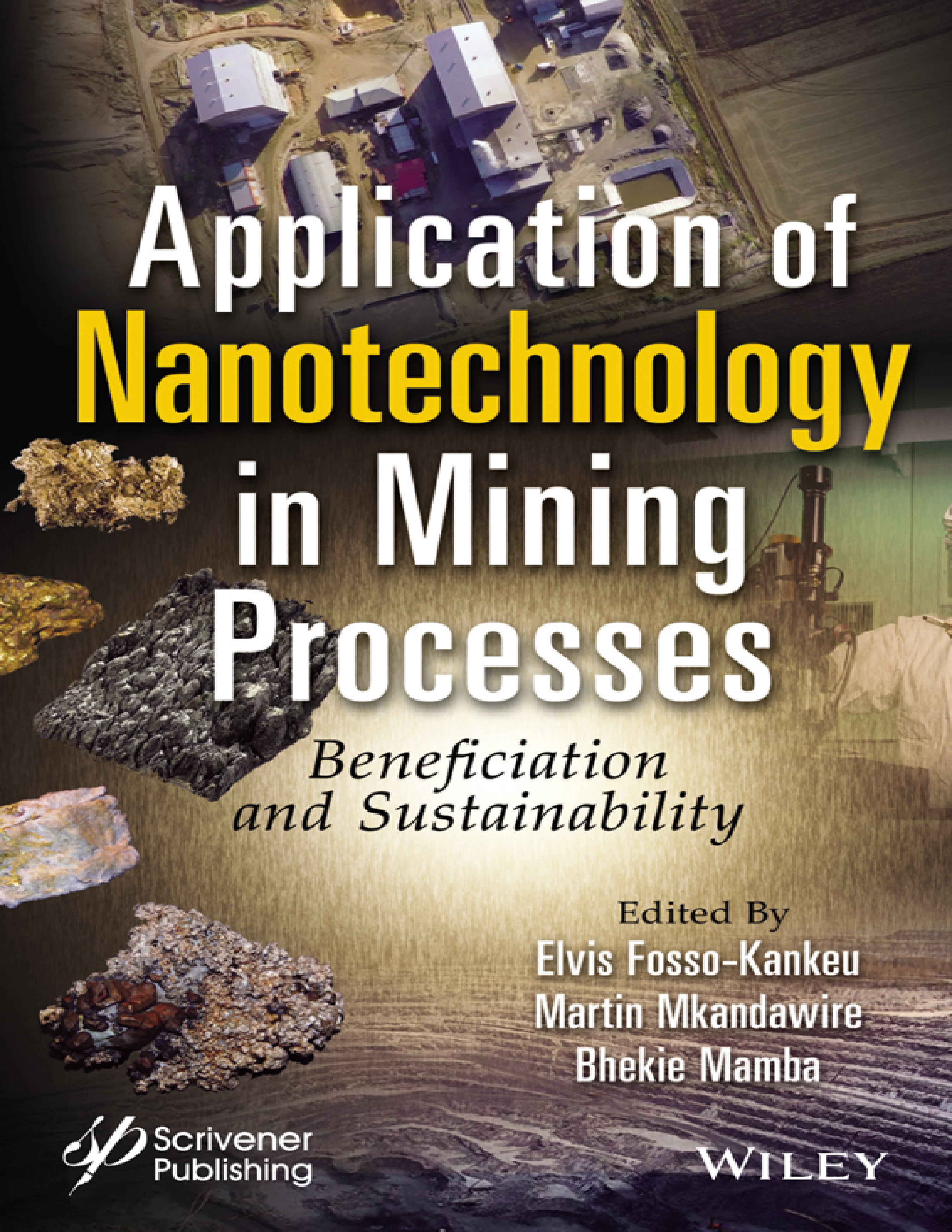

Application of Nanotechnology in Mining Processes

Beneficiation and Sustainability

Edited By

Elvis Fosso-Kankeu

Martin Mkandawire

Bhekie Mamba

Scrivener Publishing

WILEY

Table of Contents

List of Illustrations

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 9

List of Tables

Chapter 1

Chapter 7

Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Publishers at Scrivener
Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

Application of Nanotechnology in Mining Processes

Beneficiation and Sustainability

Edited by

Elvis Fosso-Kankeu
Electrical and Mining Engineering Department, University of South Africa

Martin Mkandawire
School of Science and Technology, Cape Breton University, Nova Scotia, Canada

and

Bhekie Mamba
College of Science, Engineering and Technology, University of South Africa

Scrivener
Publishing

WILEY

This edition first published 2022 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
© 2022 Scrivener Publishing LLC
For more information about Scrivener publications please visit www.scrivenerpublishing.com.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at http://www.wiley.com/go/permissions.

Wiley Global Headquarters
111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty
While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-86499-8

Cover image: Pixaby.Com
Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Preface

Nanotechnology, initially expected to revolutionize processes in industries, has affected fields in engineering in different ways. For example, the application of nanotechnology in mining processes such as minerals processing and hydrometallurgy has received limited attention so far.

Mining plays a vital role in the economic development of many countries around the world; it is, therefore, understandable that the technologies applied in mining must ensure cost-effective recovery of values from the ore and minimize the impact of processes on the environment. After extraction of ore minerals, they must be separated from the gangue to be processed for metal extraction via a process such as hydrometallurgy which is less energy demanding and has a limited impact on the environment. Although hydrometallurgy has less impact on the environment than pyrometallurgy, the former still contributes to the discharge of solid wastes containing residual sulphide minerals that can be oxidized to form acid mine drainage in the environment. However, little research has been reported on the application of nanotechnology in three mining processes, *vis* mineral processing (concentration through flotation), hydrometallurgy (concentration or purification of metals loaded solution) and management of mining liquid wastes to minimize environmental impact.

Ore minerals are generally dispersed in a large volume of gangue minerals, requiring therefore that the rock is crushed to small particles for the beneficiation of valuable minerals through froth flotation, which consists of the floatation of crushed particles in an aqueous solution containing “collector chemical” that can attach to the valuable particles allowing them to remain at the top of bubbling solution and making easier to skim them off. In conventional froth flotation, air bubbles are relatively large and less stable; recent findings have shown that the application of nanoflotation can considerably improve the separation of valuable minerals from gangue minerals through the use of hydrophobic nanoparticles or the formation of nanobubbles using special dispersing pumps.

The concentration and purification processes in hydrometallurgy often require selective extraction from solution. However, conventional techniques such as ion exchange and solvent extraction still have low efficiencies. For example, solvent extraction often results in an unpure solution due to poor coalescence of the organic solvent, which contaminates the aqueous solution, also resulting in the loss of expensive reagents. In contrast, conventional semipermeable membranes made of aggregates of polymers and ion exchangers tend to be non-selective because the absence of atomistic control limits sufficient exposure of sidechains to the solution. Recently, nanoscale supramolecular hosts exhibiting selective, high-capacity and recyclable adsorption potential have been developed and applied to extract metals from leachates or pregnant solutions with great success.

One major impact of mining activities on the environment is the formation of acid mine drainage, a very acidic solution rich in metals that can negatively affect aquatic life. One of the approaches to remediate AMD pollution often consists of removing metals using nano-adsorbents with a very large surface area and, therefore, high adsorption capacity. These nano-adsorbents are also used to extract and separate rare earth elements (REE) from mine effluents. In addition, a new approach focusing on the circular economy promotes the valorization of mine wastes such as AMD, resulting in the production of nano-based materials with economic values.

This book presents nine specialized chapters that focus on applying nanoflotation to improve mineral processing, effective extraction of metals from leachates or pregnant solutions using nanoscale supramolecular hosts, and development of nano-adsorbents or nano-based strategies for the remediation or valorization of AMD.

The editors and the publisher are grateful to the reviewers who have contributed to improving the quality of the book through their constructive comments. The editors also thank the publisher for including this book in their portfolio.

This book will be of interest to researchers from the fields of Environment, Chemistry, Engineering, Mineral processing, Hydrometallurgy and Geochemistry, engineers and environmentalists from the mining industry, as well as the environmental policies makers mostly in the public sector, to name a few. Furthermore, it is our wish that this book assists the readers in improving their experimental and operational processes by implementing the ideas disseminated in the various chapters of this book.

Elvis Fosso-Kankeu
Martin Mkandawire
Bhekie B. Mamba
January 2022

1

Modified Dendrimer Nanoparticles for Effective and Sustainable Recovery of Rare Earth Element from Acid Rock Drainage

Anyik John Leo[1,2*], Innocentia Gugulethu Erdogan[1,3], Frans B. Waanders[1], Martin Mkandawire[1,2], Thabo T.I Nkambule[4], Bhekie B. Mamba[4] and Elvis Fosso-Kankeu[4,5]

[1] *Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, North-West University, Potchefstroom, South Africa*

[2] *Solid-State Research Group, Department of Chemistry, School of Science and Technology, Cape Breton University, Sydney, Canada*

[3] *Faculty of Engineering and the Built Environment, Chemical Engineering Department, Cape Peninsula University of Technology, Cape Town, South Africa*

[4] *Institute for Nanotechnology and Water Sustainability (iNanoWS), College of Science Engineering and Technology (CSET), University of South Africa, Florida Science Campus, Johannesburg, South Africa*

[5] *Department of Electrical and Mining Engineering, College of Science Engineering and Technology (CSET), University of South Africa, Florida Science Campus, Johannesburg, South Africa*

Abstract

Mining supplies key resources necessary for technological advancement to ameliorate challenges imposed by the increase in the human population worldwide. One of the legacies of mining resources is the formation and discharge of acid mine drainage (AMD) during and even after active mining. It is a major environmental concern because it enhances the dissolution and increases the dispersion of contaminants, mostly toxic metals, in the environment. Many countries have now adopted or promulgated legislation that requires mining operators to treat and manage the formation of AMD, costing them a fortune from their profits. AMD can be an alternative source of valuable rare earth elements (REE), but the currently available extraction methods of REE from AMD are inefficient and costly, exceeding by many folds their conventional extraction from ores. Thus, there has been a growing effort to develop a novel and cost-effective method to recover REEs from AMD, in which extraction using polymeric nanomaterials, like Poly(amidoamine) (PAMAM) dendrimers, are growing in prominence. PAMAM dendrimers nanoparticles have high adsorption capacity, contributing highly to metal recovery from most wastewater. However, their application in the recovery of REEs from AMD is hampered by the low pH of the AMD, which protonates the amine functional groups forming cationic charges on the surfaces of the dendrimer nanoparticles. Therefore, designing these materials to adsorb metal ions in an acidic solution is paramount for treating AMD. This chapter discusses designing a cost-effective method for the recovery of REEs from AMD after alkaline treatment, using surface-functionalized magnetic PAMAM dendrimer nanoparticles. The environmental effect and shortcomings of AMD remediation methods will be highlighted as a background motivation in developing this procedure.

Keywords: Acid rock drainage, dendrimers, magnetic iron oxides nanoparticle, potentially toxic elements, rare earth element

1.1 Introduction

The global human population has risen considerably since the industrial revolution and currently stands at above 7.7 billion worldwide, beyond the carrying capacity of the earth [1]. The rapid population growth is imposing tremendous challenges such as the easy spread of disease outbreaks, food scarcity, shortage of infrastructures, and insufficient communication networks, which require resources and technological advancement to ameliorate these predicaments. All resources required for this technological advancement come from mother earth and can be obtained only through two means; if they cannot be harvested (from farming), they should be mined. The mining industry plays a vital role in supplying these key resources but lacks the potential to obtain mineral resources without compromising environmental integrity [2]. Nevertheless, mining cannot be easily halted due to the growing need for mineral resources to support technological advancement required to artificially sustain the ever-increasing human population, which is beyond the earth’s carrying capacity. The mineral resources, including metals, are essential components in the advancement of several technologies, like the production of medications and vaccines, fertilizers for agricultural application to ensure food security, and the manufacture of building materials for construction of mega-infrastructures to improve road networks. They are also used as vital components to manufacture computers and cell phones for better communication networks. In addition, mining is a vital economic activity for many nations, bringing in much-needed foreign exchange earnings and employment [3]. Despite the benefits mentioned above, the legacy of mining activities includes major environmental pollution and heaps or piles of municipal solid waste (MSW) from mining [4]. For example, most valuable minerals like gold (Au), copper (Cu), sulfur (S), zinc (Zn), silver (Ag) or lead (Pb) occurs in sulfidic ore bodies (Table 1.1) with more than one type of mineralization [5]. Once these valuable metals have been extracted from their sulfidic ores, vast volumes of mine water and leftover mining solid wastes and tailings are generated, which contain most of the sulfide mineral, like pyrite. The exposure of the pyrite-containing waste to oxygen and water leads to an acid-generating material, producing acid mine drainage (AMD). The discharge of AMD is attributed to most of the contamination being transported from mining sites to the receiving environments, affecting environmental water quality [6–8] (Figure 1.1). Due to its well-known and publicized ecological impacts, many countries have adopted stringent regulations, such as Section 402 of the Clean Water Act of the Republic of South Africa, enabling mining operators to treat mine water discharging AMD [9–11].

On the one hand, treatment of AMD as required by environmental legislation has serious financial implications for the mining operators, but on the other hand, generation of AMD in former mining sites occurs long after active mining when the responsible mining companies no longer exist. Thus, treatment and remediation of AMD are an economic and financial burden to the mining company if the operation is still active, and to the community and their governments in closed or abandoned mines. Mine water discharging AMD is known to contain a consortium of dissolved elements, including precious metals and rare-earth elements (REE) [12]. Thus, AMD can be a valuable resource, especially of REE and precious metals that can generate more income and compensate for the treatment and remediation expenses of mine water and contaminated mining sites [13]. Furthermore, AMD can be regarded as an initial and natural process of hydrometallurgy of REE. However, extraction of REE from AMD is a big challenge due to the need for highly selective extraction methods, targeting only REE and leaving other metal ions dissolved in AMD to produce the required purity. Thus, recovery of REE from AMD is usually more expensive, resulting in AMD not being attractive as a source of REE. Nevertheless, using polymeric nanomaterials as hydrometallurgical extraction agents is promising to be a cost-effective and efficient method of extracting REE from AMD. One of the agent groups with high potential is Poly(amidoamine) (PAMAM) dendrimers. Consequently, this chapter discusses the application of PAMAM dendrimers as an extraction agent of REE, evaluating their performance potential and the development of methods in which they are applied.

Table 1.1 Different types of sulfide-bearing ore bodies, % content in ore body, uses, world deposit and origin [14, 15].

Sulfide ore bodies and formula	**Minerals present in the ore body with % content**	**Application of the major elements in the ore body**	**Regions of major deposit of ore bodies in the world**	**Origin of occurrence**
Arsenopyrite **($FeAsS$)**	Arsenopyrite is the major source of arsenic, with 46% Arsenic, 34.3% Iron, and 19.7% Sulfur in the ore body. It should be noted that the arsenic content is made up of minor gold deposits.	Used in the manufacture of herbicide, alloys, wood preservative, medicine, insecticide, and rat poison.	China, Morocco, Namibia, Russia, Belgium, Iran, and Japan	Hydrothermal veins, pegmatite, contact metamorphism, and metasomatism
Bornite **(Cu_5FeS_4)**	Source of rich-grade copper metal. The ore body contains 63.3% Copper (Cu), 11.1% Iron (Fe), and 25.6% Sulfur (S)	Major applications are in electrical wires, cables, plumbing, currency, utensils, machinery, alloys, architecture, nutritional supplements, and agricultural fungicides	United States, England, Austria, Zimbabwe, Morocco, Dzhezkazgan, and Kazakhstan	In the zone of secondary supergene enrichment, source of rich copper metal
Chalcopyrite **($CuFeS_2$)**	Chalcopyrite is the principal source of copper metal and accounts for	Major applications of copper metal are in electrical wires, cables, plumbing, currency,	Chile, China, Peru, United States, DRC, Australia, Russia, Zambia,	Large, massive, irregular veins, disseminated and porphyry deposit at granitic/dioritic

	approximately 70% of the copper deposits in the world. The ore body content is made up of 34.5% Copper (Cu), 30.5% Iron (Fe), and 35.0% Sulphur (S)	utensils, machinery, alloys, architecture, nutritional supplements, agricultural fungicides, and space exploration capsules	Canada, and Mexico	intrusive and SEDEX type
Cinnabar (**HgS)**	The ore body is a primary source of mercury. It contains 86.2% Mercury (Hg) and 13.8% Sulfur (S).	Used in the manufacturing of industrial chemicals and in electronics, thermometers, medicine, cosmetics, pigments, and fluorescent lamps. Environmentally sensitive due to health and safety regulations	China, Mexico, Kyrgyzstan, Peru, and Tajikistan	Vein-filling by recent volcanic activity and acid-alkaline hot spring
Galena **(PbS)**	Galena is the primary source of lead metal and one of the sources of sulfur. It contains 86.6% Lead (Pb) and 13.4% Sulfur (S).	Used as a key ingredient for paint production, used in plumbing materials, bullets, automobile batteries, alloys, sheets, radiation shields, electrodes, ceramic glazes, stained glass, and cosmetics	China, Australia, United States, Peru, Russia, Mexico, and India	Individually or associated with zinc and copper sulfide deposit
Molybdenite	The primary	Used to coat	Armenia,	High-

(MoS_2)	source of molybdenum with 60% Molybdenum (Mo) content and 40% Sulfur (S)	stainless steel materials because it is resistant to corrosion, used as lubricant, tools, and high-speed steels, cast iron, electrodes, fertilizers, and for pollution control in power plants	Canada, Chile, China, Iran, Mexico, Mongolia, Peru, Russia, and United States	temperature hydrothermal ore of chalcopyrite, pyrite, and molybdenite
Pentlandite **($(Fe, Ni)_9S_8$)**	The primary source of nickel with 22% Nickel (Ni), 42% Iron (Fe), and 36% Sulfur (S)	Used in stainless steel, superalloys, electroplating, alnico magnets, coinage, rechargeable batteries, electric guitar strings, 4.6 microphone capsules, and green tinted glass	Australia, Namibia, Canada, and Brazil	The layered maficultramafic intrusion at high magmatic temperature, differential segregation
Pyrite **(FeS_2)**	Common in all rocks and as massive sulfide deposits. It contains 46.6% Iron (Fe) and 53.4% Sulfur (S)	Mainly used to produce sulfur dioxide for paper and sulfuric acid for the chemical industry. Rarely mined for iron content due to complex metallurgy and being uneconomical commercially. Acid drainage and dust explosion are common hazards	Italy, Spain, Kazakhstan, and United States	Common in all rocks, and as massive sulfide deposits associated with gold

		with pyrite deposits.		
Sphalerite **(ZnS)**	The primary source of zinc with 67% Zinc content and 33% Sulfur (S)	The main applications are in galvanizing, alloys, cosmetics, pharmaceuticals, 3.9 micronutrients for humans, animals, and plants	China, Peru, Australia, United States, Mexico, India, Bolivia, Kazakhstan, Canada, and Sweden	The majority as large SEDEX-type deposits associated with galena, chalcopyrite, and silver

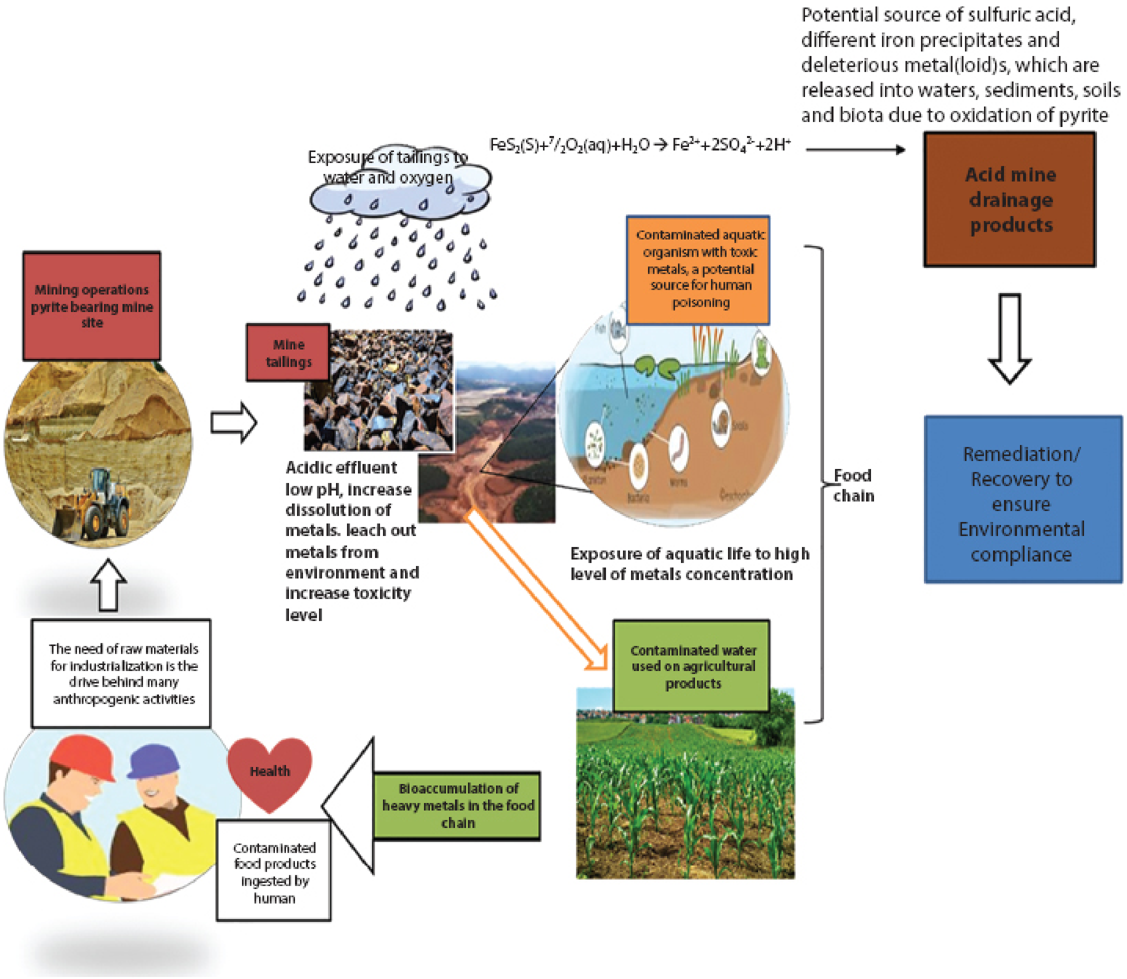

Figure 1.1 Schematic showing the pathway of AMD formation, its dispersion into the environment and entrance into the food chain: The destruction of natural vegetation in search of mineral resources exposes large surface areas to weathering effects. Due to the presence of sulfide materials in these mine tailings, AMD products are formed which can be washed away into nearby streams. Aquatic life suffers the consequences due to an increase in mortality rate; meanwhile, these polluted waters can be used for irrigation and thus will bioaccumulate in plants. Once in the food chain, human lives are affected in the process.

1.2 Rare-Earth Element Occurrence in Acid Mine Drainage

1.2.1 Acid Mine Drainage Generation and Effects

Although the formation of AMD has been historically attributed to mine tailing dams containing sulfide-bearing materials, it can occur naturally in an environment that exposes hefty volumes of sulfide-bearing materials to air and water [16]. However, of the different sulfide ore deposits shown in

Table 1.1, pyrite is the most common and by far the most abundant sulfide mineral [17]. Using pyrite as an example for the generation of AMD, the oxidation process is represented by different reactions (1–3) [18]. Pyrite is oxidized to sulphate ions (SO_4^{2-}), ferrous iron (Fe^{2+}) and protons (H^+) at the initial stage when the tailing dam is exposed to atmospheric oxygen in the presence of excess water at neutral pH (1.1).

$$FeS_2(S)+\frac{7}{2}O_2(aq)+H_2O\rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \tag{1.1}$$

The formation of Fe^{2+} is solubilized by the oxidation process and subsequently oxidized to ferric iron (Fe^{3+}) and is the rate-determining step of the overall reaction (1.2).

$$Fe^{2+}+\frac{1}{4}O_2+H^+\rightarrow Fe^{3+}+\frac{1}{2}H_2O \tag{1.2}$$

Ferric cations produced can also oxidize additional pyrite into ferrous ions, and the net effect of these reactions is to produce H^+, which increases the acidity of the influent and maintains the solubility of the ferric iron (1.3).

$$FeS_2(S)+14Fe^{3+}+8H_2O\rightarrow 15Fe^{2+}+SO_4^{2-}+16H^+ \tag{1.3}$$

The pH value of AMD is as low as 2–4 and will naturally enhance the rate of dissolution of potentially toxic elements (PTEs), resulting in the tailing dam containing a high content of metal(loids), including sulfate ions in solution. Once leached into the lotic system (river), it will destroy their bicarbonate buffering system and enhance the rate of dissolution of metal ions, which could persist for hundreds of years once initiated, forming an age-long pollution stream with low pH [5, 19]. Consequently, the design lifespan of civil infrastructures such as water reticulation networks and bridges within this environment are shortened, caused by corrosion when metal oxides are formed [20]. In addition, the mortality rate of the aquatic organism within this inhospitable environment increases once these toxic metals accumulate in their organs [21]. More so, when this polluted water enters the irrigational system, the toxic metals accumulate in plants and indirectly enter the food chain. The growth of plants is distorted because, at low pH, plant nutrients such as nitrogen, phosphorus, and potassium necessary for their growth are immobilized, and the calcium and magnesium content becomes deficient. Meanwhile, in the food chain, these toxic metals bioaccumulate and cause deleterious health effects in humans (Table 1.2) due to their non-biodegradability [22, 23].

Table 1.2 Potential toxic elements and their effect in humans.

Elements	**Recommended levels in surface or groundwater (ppm)**	**Health-related issues in humans**	**Reference**
Aluminum (Al)	2.9	Aluminum exposure is a risk factor for the development or acceleration of the onset of Alzheimer's disease (AD) in humans.	[33]
Arsenic (As)	0.01	Exposure to arsenic causes skin and internal organ cancers, impaired nerve function, kidney and liver damage, or skin lesions.	[34]
Copper (Cu)	2.0	Exposure to excess copper induces oxidative stress, DNA damage and reduced cell proliferation in the human body.	[35]
Iron (Fe)	1.0–3.0	Iron is an essential part of hemoglobin in humans, but its overload causes severe health problems such as liver cancer, diabetes, cirrhosis of the liver, heart diseases and infertility.	[36]
Manganese (Mn)	0.5	Manganese is an essential nutrient to the body, but in excess can also interfere with the normal function of the nervous system to induce motor and cognitive impairments as well as neuropsychiatric symptoms.	[37]
Lead (Pb)	0.01	Exposure to lead causes cardiotoxicity, neurotoxicity, nephrotoxicity, carcinogenicity and genotoxicity in humans.	[38]
Zinc (Zn)	5.0	Zinc is considered an essential mineral in humans as it is necessary to produce hundreds of enzymes throughout the body. The toxicity of Zn in humans differs significantly and varies from acute exposure to chronic exposure.	[39]

		Renal injury, ranging from asymptomatic hematuria to interstitial nephritis or acute tubular necrosis, has also been reported due to acute toxicity, while chronic exposure can lead to sideroblastic anemia and granulocytopenia, and myelodysplastic syndrome.	
Rare earth elements (REEs)	Data not established and are currently unregulated in humans and environment	Despite their extensive application in electronics, exposure to these metals will cause dysfunctional neurological disorders such as reduced intelligence quotient (IQ) in children, bone alteration, genotoxicity and fibrotic tissue injury and antitesticular effects and male sterility in humans.	[40]